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## XIII. STUDIES ON THE SOILS OF THE NORTHERN PORTION OF THE GREAT PLAINS REGION: THE THIRD STEPPE.

BY FREDERICK J. ALWAY AND ROSS A. GORTNER.

The third steppe extends from the Missouri Coteau westward to the Rocky Mountains or the bordering foot-hills, including the portions of Alberta and western Saskatchewan south of the North Saskatchewan River. The altitude varies from about 2100 feet on the east to over 4,000 feet at the foot of the mountains. The greater part of the steppe is almost entirely devoid of forest. Cacti and other xerophytic plants attest to the arid character of the southern portion. Numerous alkali lakes without outlets serve as evaporating basins for a large part of the run-off. The analysis of water from the largest of these, Old Wives Lake, is given below. Its chief constituent is sodium sulphate. The mean winter temperature on this steppe rises steadily in passing from east to west. The proportion of bright sunshine is high; in connection with this it is interesting to note the deep violet color acquired by

colorless glass that has been exposed, for some time, upon this steppe, to the sunshine. The nature of the soil is too varied to admit of generalizations. There are considerable areas of bare drifting sand-hills and tracts of barren, stiff clay of the typical Bad Lands character, as well as the more extensive, fertile, grass-covered plains. In general, the soil is more sandy and gravelly than that of the second steppe. The soils analyzed were taken from the wide, grassy plain at the western border. The surface soils are rich in nitrogen, potash and lime and are well provided with phosphoric acid. The subsoil differs in mineral constituents from the preceding chiefly in the much larger amount of calcium and magnesium carbonates and in a somewhat smaller amount of potash. Both contain considerable quantities of water-soluble salts, which in many places over the area have been partly leached out into the depressions, forming tracts of alkali-lands. The composition of the samples agrees with the generalizations made by Hilgard[1] in regard to the relations of soils to climate. The rather large proportion of manganese in the subsoil doubtless bears no relation to the change in the color of the glass lying on the surface.

*Analysis of Water from Old Wives Lake.*

This lake, which is 2,165 feet above sea-level and lies near the eastern edge of the steppe, serves as an evaporating basin for the drainage of a region about 5,000 square miles in area. Its composition will, accordingly, indicate the nature of the water-soluble salts occurring in the soil over a considerable part of the steppe. The lake is divided into two parts, a southern, called Lake Johnston, and a northern, Lake Chaplin. The two are connected by a channel 10 miles in length, which serves to keep the surface of the two divisions at the same level. All the creeks, which feed the lake, unite to form Old Wives Creek, which empties into the channel near its southern end. Differences in the composition of the water of the two portions of the lake are likely to be confined to the concentration of dissolved salts and not to extend to the relative proportions of these.

1 Wollny's "Forschungen," 16, 51–91.

The sample of water used in this analysis was collected by one of the writers, near the northern shore of Lake Chaplin and near the railway station of the same name, in July, 1904. At the time of collection the water emitted a distinct odor of hydrogen sulphide and carried only traces of suspended matter. The sample was so small that some of the constituents were not determined.

The sp. gr. of the water at 15° was 1.018. The weight of solids, dried at 180°, was 27.7055 grams per liter.

Analysis:

| | Grams per liter. | Total inorganic material in solution. Per cent. |
|---|---|---|
| Sodium (Na) | 8.3674 | 30.20 |
| Potassium (K) | trace | . . |
| Calcium (Ca) | " | . . |
| Magnesium (Mg) | 0.2677 | 0.96 |
| Aluminium (Al) | trace | . |
| Chlorine (Cl) | 1.3623 | 4.91 |
| Carbonate ($CO_3$) | 0.4200 | 1.52 |
| Sulphate ($SO_4$) | 16.8883 | 60.96 |
| Silicate ($SiO_3$) | trace | . . |
| Total | 27.3057 | 98.55 |

*Analysis of Surface Soil and Subsoil.*

The samples analyzed were taken by one of the writers in April, 1906, from near Gleichen. The surface soil, to a depth of 12 inches, was secured from several different places and thoroughly mixed for sample No. 1. No. 2 was prepared by mixing 100 gram portions of each foot section, from the second to the sixth, obtained from 2 borings. The method of analysis employed was that of Hilgard.[1] A weighed quantity of fine material, below 0.5 mm. in diameter, which had been dried at 100°, was placed in a porcelain beaker, covered with a watch glass, treated with from 8–10 times its bulk of hydrochloric acid, sp. gr. 1.115, and a few drops of nitric acid, and digested for 5 days over a steam bath.

[1] Cal. Agr. Expr. Station, Circular 6 (1903).

| | No. 1. Surface soil. | | No. 2. Subsoil. | |
|---|---|---|---|---|
| Insoluble matter | 62.85 | 77.99 | 60.67 | 73.02 |
| Soluble silica | 15.14 | | 12.35 | |
| Potash ($K_2O$) | | 1.29 | | 0.84 |
| Soda ($Na_2O$) | | 0.33 | | 0.29 |
| Lime (CaO) | | 1.03 | | 6.43 |
| Magnesia (MgO) | | 0.71 | | 1.70 |
| Brown oxide of manganese ($Mn_3O_4$) | | 0.07 | | 0.22 |
| Peroxide of iron ($Fe_2O_3$) | | 4.61 | | 3.31 |
| Alumina ($Al_2O_3$) | | 5.17 | | 4.50 |
| Phosphoric acid ($P_2O_5$) | | 0.16 | | 0.15 |
| Sulphuric acid ($SO_3$) | | 0.67 | | 0.12 |
| Carbonic acid ($CO_2$) | | 0.39 | | 5.68 |
| Water and organic matter | | 7.75 | | 3.60 |
| Total | | 100.17 | | 99.86 |
| Nitrogen | | 0.22 | | . . |
| Hygroscopic coefficient at 10° | | 5.7 | | 4.5 |

The soil was evidently of lacustral origin, being free of stones or gravel and being underlaid by boulder clay.

*The Action of Sunshine upon Colorless Glass Exposed upon the Third Steppe.*

After glass objects, that were originally colorless, have been exposed for some time to the direct sunshine upon this steppe, their appearance is quite remarkable. Apparently they all soon assume a more or less intense violet coloration. This color is in very many cases sufficiently intense to be easily recognizable from the windows of a moving train. Deeply colored glass bottles or broken pieces of glass were observed by one of the writers, at frequent intervals, all the way from Calgary, on the extreme western edge of the steppe, to the eastern border at the Missouri Coteau. A few less strongly colored specimens were found at Moose Jaw, on the second steppe. As the ground at the last-mentioned place was covered with snow at the time and thus obscured nearly all glass objects that had been exposed to the sunshine, it would not be justifiable to conclude that glass exposed on the western part

of the second steppe will differ in the extent of the color change from that lying, under similar conditions, on the eastern part of the third steppe.

At the village of Gleichen, and at the city of Calgary there are large quantities of glass on the garbage grounds. These were examined in the hope of finding colorless glass that bore evidence of long exposure, or glass, originally of a faint greenish shade, that had acquired a violet tint. In no case was ordinary window glass, or a glass jar or bottle showing a greenish color on broken edges, found to have acquired any violet coloration. Window panes that had been exposed to the direct sunshine for many years, as well as large heaps of broken window glass upon the surface of which were violet colored glass objects, were examined with the result that only a single piece, part of a pressed window pane of colorless glass, which showed a bluish-green color on the broken edges, was observed, that seemed an exception. Several pieces of this pane were found, those on the top of the heap being quite violet, even on the broken edges, while those buried in the heap, and so protected by the overlying ordinary window glass, were free from any violet tint. On analysis it was found to contain a large amount of manganese. All the specimens of colorless glass found gave evidence of not having been long exposed or of having been protected from the direct rays of the sun by soil or rubbish. The articles were of the most varied description, lamps, lamp-chimneys, tableware, medicine, pickle and preserve bottles. That the time of exposure of many of the violet colored bottles had not been long was evident from the almost perfect condition of the gummed paper labels. Violet colored glass, lying on grass of last season's growth, was observed on the prairie so frequently, and so far removed from any accumulation of glass, that it was necessary to conclude that the coloration had taken place since the close of last summer, *i. e.*, within 8 or 9 months. In none of these instances, of evidently brief exposure, was the maximum coloration observed.

While it has long been known that glass, decolorized by means of manganese compounds, gradually acquires a violet shade on long exposure to the direct sunlight, it does not seem to

have been recognized until recently that the coloration may become apparent within a few years. Crookes[1] called attention to the subject in a description of some violet colored specimens of glass found in Bolivia at a considerable altitude, over 13,000 feet, and in a region of much bright sunshine. Fischer[2] has shown that the cause of this violet coloration is due to the action of the ultraviolet rays and can be produced within 12 hours by exposure to the rays from a mercury lamp, in glass containing readily recognizable amounts of manganese, while no change takes place in glass practically free from manganese. Similarly colored glass, from New Mexico, was reported by Avery,[3] who found considerable quantities of manganese in the specimens. This writer found, further, that the intensity of the coloration was approximately proportional to the manganese content. Simpson[4] observed glass prisms in West Australia to show a violet coloration after an exposure of between 1 and 2 years. Ruger,[5] finding colored glass at Butte, Montana, suggested that the violet color might be connected with the presence of manganese compounds, which occur in large quantities in the vicinity. From no other region, however, has such a wealth of specimens been reported as is to be found on the second prairie steppe of Canada.

After a long and careful search we have found a considerable number of violet colored specimens within a few miles of this university. The color, however, is faint compared with that of many of the specimens from Gleichen and Calgary. The most interesting specimen found here is a colorless glass bottle, which on August 26, 1905, was thrown by one of the writers upon a pile of stones. On May 1, 1906, a large piece of the bottle, lying on the top of the pile and fully exposed to the sunshine, was found to be distinctly colored violet. The other pieces of the bottle had fallen among the stones and were less strongly colored, some, that had been protected, being quite colorless. A qualitative test showed the presence of a very large amount of manganese.

[1] Chem. News, 91, 73 (1905).
[2] Ber. d. Chem. Ges., 38, 946 (1905).
[3] J. Am. Chem. Soc., 27, 909 (1905).
[4] Chem. News, 91, 236 (1905).
[5] J. Am. Chem. Soc., 27, 1206 (1905).

In view of the above, it seems safe to conclude that varieties of colorless glass containing appreciable quantities of manganese may assume a violet tint, after an exposure to the sunshine of less than a year, both near the northwestern limit and near the eastern border of the great plains, independent of the altitude and of the temperature. It is probable that similar specimens will be found over the whole of the great plains region, the coloration being most intense in those from the western portions.

UNIVERSITY PLACE,
NEBRASKA,
July, 1906.

**Contributions from the Chemical Laboratory of Harvard College.**

## ON CERTAIN DERIVATIVES OF TETRACHLORORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND R. D. MACLAURIN.

After much time had been devoted in this laboratory to the study of the reactions of tetrabromorthobenzoquinone,[2] it seemed of interest to determine whether the tetrachlororthobenzoquinone behaved in the same way; and in the present paper we describe the first part of our work on this subject.

We prepared tetrachlororthoquinone, discovered by Zincke,[3] by a method similar to that given by him, which yielded good results, if certain precautions were carefully observed. In this way it was obtained as a bright red substance, melting at 133° to a dark red liquid. Zincke and Küster[4] give its melting point as 129°–130°.

The tetrachlororthoquinone is converted by tetrachlorpyrocatechin into the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, which differs from the corresponding hexabrom compound[5] in having a lighter red color, melting at 300°, whereas the brom compound does not melt within the range

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Robert D. MacLaurin.

[2] THIS JOURNAL, **26**, 10; **30**, 518; **31**, 89; **34**, 422, 460; **35**, 154.

[3] Ber. d. chem. Ges., **20**, 1779 (1887).

[4] *Ibid.*, **21**, 2730 (1888).

[5] Jackson and Koch: THIS JOURNAL, **26**, 35 (1901).

of the thermometer, and being more soluble in the organic solvents, although it is still a slightly soluble substance.

By reduction with sodium amalgam and water the orthoquino ether is converted into the hexachlordihydroxypyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2(OH)_2$, which resembles the hexabrom compound[1] in crystallizing from alcohol in white needles, from other solvents in brown crystals, and by showing a surprisingly slight solubility in aqueous sodic hydrate; but it has a melting point 290°, instead of remaining unfused at temperatures within the range of the thermometer, and is more soluble in the common solvents. During the reduction of the hexachlororthoquinopyrocatechin ether a small amount of it is decomposed into substituted pyrocatechins, so that in this respect it also resembles the hexabrom compound.

In both these cases, therefore, the chlor compound resembles the corresponding one containing bromine with only such slight differences as would be expected. The same is true of the action of tetrachlororthoquinone on aniline dissolved in alcohol, as this yielded 4 products, the melting points of which are compared with those of the corresponding brom compounds in the following table:

| | Cl. | Br. |
|---|---|---|
| $C_6X_2(C_6H_5NH)_2O_2$ | 194°–195° | 160° |
| $C_6X_2(C_6H_5NH)_2O_2.C_6H_5NH_2$ | 164°–165° | 121°–124° |
| $C_6X_2(C_6H_5NH)_2O_2.C_2H_5OH$ | 140°–141° | 142° |
| $C_6HX(C_6H_5NH)_2ONC_6H_5$ | 180° | 173° |

That the last 2 compounds belong to the para series is shown by the fact that sulphurous dioxide, in ethereal solution, converts them into dianilinoparaquinoneanil,

$$C_6H_2(C_6H_5NH)_2ONC_6H_5,$$

as such a mild reaction carried on in the cold could not have brought about the change from the ortho to the para series. This inference is confirmed by the observations that the substance melting at 180° gives no addition compounds, and that sulphuric acid forms a purple solution with it, whereas it gives a green color with all the dianilinoorthoquinones studied. Conversions of ortho into paraquinones are far from uncommon.

[1] Jackson and Koch: *Ibid.*, **26**, 39 (1901). Jackson and Porter: *Ibid.*, **30**, 523 (1903).

The dianilinoparaquinoneanil was also formed by boiling any of the chlor compounds mentioned in the table with aniline and alcohol for 3–4 days, but this reaction is of no value in determining the constitution of these bodies, as the change from the ortho to the para series might well have taken place during this long process. As in previous work in this laboratory, great difficulty was experienced in raising the melting point of the dianilinoparaquinoneanil to 202°–203°. We therefore contented ourselves with proving the identity of our product by comparison with known samples of that body.

The behavior of the aniline dianilinodichlororthoquinone toward solvents is somewhat peculiar; from benzene alone it crystallizes unaltered, but a mixture of 5 parts of benzene with 1 of ligroin decomposes it into dianilinodichlororthoquinone and aniline. The probable explanation of these observations is that the aniline compound is dissociated by solution, and its 2 constituents recombine to form it once more, when both remain in the saturated solution, from which crystals are forming, whereas, the ligroin rendering the dianilinodichlororthoquinone insoluble, precipitates it, thus removing it from the possibility of reuniting with the dissolved aniline.

The conversion of the dianilinodichlororthoquinone,

$$C_6Cl_2(C_6H_5NH)_2O_2,$$

into dianilinochlorparaquinoneanil,

$$C_6HCl(C_6H_5NH)_2ONC_6H_5,$$

and of this latter body into the anil,

$$C_6H_2(C_6H_5NH)_2ONC_6H_5,$$

are noteworthy, because in these cases chlorine attached to a benzene ring has been replaced by hydrogen under the influence of hot aniline and alcohol, and this recalls the similar replacements of bromine or iodine in aromatic compounds under the influence of sodic alcoholates, sodic acetacetic ester, or sodic malonic ester, which have long been a subject of study in this laboratory. So far as we are aware only one other case is known in which chlorine has been replaced by hydrogen under such conditions. Gazzolo and one of us[1] obtained

[1] THIS JOURNAL, **22**, 58 (1899).

bromdiethoxydinitrobenzene from trichlorbromdinitrobenzene treated with sodic ethylate. In all other cases studied the chlorine either underwent a normal replacement, or remained unaltered. It is, therefore, an interesting point that the chlorine in this case is removed with much greater difficulty than bromine in the corresponding compound, for whereas the dianilinobromparaquinoneanil is deprived of its bromine by boiling with aniline and alcohol for 2–4 hours, the chlorine is fully replaced by hydrogen only after boiling for 3–4 days with the same mixture, and what makes this the more striking is that our other work with tetrachlororthoquinone, to be described in a later paper, shows that in substituted orthoquinones chlorine is much more easily replaced than bromine by radicals other than hydrogen. Whether this reduction of the halogen compound is due to the aniline, or to the alcohol, the aniline in this latter case acting only as a weak base, must be determined by further experiments.

The tetrachlororthoquinone also acted like the tetrabrom compound when it was treated with benzaldehyde, or acetone. Three compounds were formed in each case, a yellow, a red, identified as hexachlororthoquinopyrocatechin ether, and brown hexachlordihydroxypyrocatechin ether. Russe and one of us[1] found that the tetrabromorthoquinone with various ketones and aldehydes gave, in each case, only 3 products, the 2 hexabrom ethers, and the yellow hemiether,

$$C_6Br_4(OH)O.C_6Br_3O_2.$$

There is little doubt that our yellow product is the heptachlorhemiether, $C_6Cl_4(OH)O.C_6Cl_3O_2$, but it would be extremely difficult if not impossible to prove this, as even washing it with alcohol, or ligroin converts it into the ether,

$$C_6Cl_4O_2.C_6Cl_2O_2,$$

a result which is in harmony with our observation that chlorine is removed from these substituted orthoquinones more easily than bromine.

On one occasion, when an excess of chlorine was used in the preparation of tetrachlorpyrocatechin, we obtained what

[1] THIS JOURNAL, 36, 163 (1906).

seemed to be a new quinone. Zincke and Küster,[1] under somewhat similar conditions, obtained the hexachlordiketotetrahydrobenzene, but our substance could not be identical with this, as it melted at 146°–147° instead of at 93°–94°, and a single chlorine determination indicated that it had the formula $C_6HCl_5O_2$. If this result is confirmed by further determinations it would be called pentachlordiketotetrahydrobenzene. We hope that the investigation of this substance may be continued in this laboratory in the near future.

## EXPERIMENTAL.

*Preparation of Tetrachlororthobenzoquinone.*—The tetrachlorpyrocatechin used by us was prepared as follows, very nearly according to the method of Zincke:[2] Forty grams of pyrocatechin were dissolved in 200 cc. of glacial acetic acid in a 500 cc. flask, and treated with chlorine washed free from hydrochloric acid and dried with sulphuric acid. The stream of chlorine should not be too rapid, and the solution of pyrocatechin should be kept at temperatures below 30° by immersion in a vessel of water. If the process ran properly, the liquid took on a deep red color after 2 hours, and then the continued addition of the chlorine for a few minutes caused the mixture to become nearly solid, from the separation of crystals of tetrachlorpyrocatechin. These were filtered out, and the mother liquor treated again with chlorine, when a second crop of crystals was obtained, while a third treatment of the mother liquors with chlorine gave still another mass of crystals. The yield was nearly quantitative. It was purified by 2 crystallizations from glacial acetic acid, followed by washing with very dilute alcohol, or by crystallization from dilute alcohol, when it melted at 194°. If, in the foregoing preparation, the temperature of the solution was allowed to rise above 70° during the third hour of the addition of chlorine, its color changed from red to yellow, and hexachlororthodiketotetrahydrobenzene was formed. The tetrachlorpyrocatechin was converted into tetrachlororthoquinone by a method similar

[1] Ber. d. chem. Ges., **21**, 2723 (1888).
[2] *Ibid.*, **20**, 1770 (1887).

to that used by Koch and one of us[1] for making tetrabromorthoquinone. Thirty grams of tetrachlorpyrocatechin were dissolved in 200 cc. of glacial acetic acid with the aid of heat. The solution was then cooled by placing it in ice, until crystals began to form, when 11 grams of fuming nitric acid, diluted with 60 cc. of glacial acetic acid, were added gradually, and the mixture stirred rapidly for 90 seconds, after which it was diluted with 500 cc. of ice-cold distilled water, and thoroughly stirred again. In the course of 10 minutes bright red flakes of the quinone settled at the bottom of the beaker, when the supernatant liquid was siphoned off and the solid thrown upon a paper filter, supported in the funnel by a perforated porcelain plate covered with a thin asbestos mat, so that all the filtrations could be carried on by suction as rapidly as possible. After the mother liquor had been removed, the crystals were washed with 5 successive portions of 20 cc. of water, each wash water being thoroughly removed before adding the next, and then dried at 60°–70°, when they appeared as a bright red powder, melting at 133° to a dark red liquid. This melting point is higher than 129°–130°, that given by Zincke and Küster.[2] In this way 24.2 grams of tetrachlororthoquinone were obtained from 30 grams of tetrachlorpyrocatechin, *i. e.*, over 81 per cent of the theoretical yield. The success of this preparation was found to depend on the observance of the following conditions: Careful purification of the tetrachlorpyrocatechin, keeping the amounts of glacial acetic acid and water as small as possible, since the product is somewhat soluble in water, and rapid and complete filtration.

*Hexachlororthoquinopyrocatechin ether*, $C_6Cl_4O_2.C_6Cl_2O_2$.—This substance was prepared by the method[3] which had yielded the hexabrom ether. Eleven grams of tetrachlororthoquinone and 10 grams of tetrachlorpyrocatechin, dissolved in 300 cc. of glacial acetic acid by warming on the steam bath, were mixed with 150 cc. of water, and the mixture gently heated. The

[1] THIS JOURNAL, **26**, 34 (1901). Zincke and Küster: Ber. d. chem. Ges., **21**, 2729 (1888).

[2] Ber. d. chem. Ges., **21**, 2729 (1888).

[3] Jackson and Koch: THIS JOURNAL, **26**, 35 (1901).

brilliant red precipitate formed in this way was filtered out, washed with alcohol, dried and found to weigh 13–14 grams, so that the yield of crude ether was about 76–80 per cent of the theoretical. It was purified by 2 crystallizations from nitrobenzene, when it showed the constant melting point 300°; it was then washed with alcohol to remove adhering nitrobenzene, and dried at 100° for analysis.

0.1666 gram substance gave 0.3392 gram AgCl.

| | Calculated for $C_6Cl_4O_2.C_6Cl_2O_2$. | Found. |
|---|---|---|
| Cl | 50.59 | 50.34 |

*Properties of Hexachlororthoquinopyrocatechin Ether.*—It crystallizes from benzene, in which it is only sparingly soluble, in bright red needles; from nitrobenzene in red, truncated pyramids, but its color is lighter than that of the corresponding bromine compound. It melts at 300°, and is slightly soluble in most of the organic solvents. The best solvent for it is nitrobenzene, but the solution must not be heated much above 100°, as at high temperatures the ether is decomposed with the formation of a brown product. The strong mineral acids have no effect on it, but sodic or potassic hydrate converts it into the corresponding salt of chloranilic acid. Aqueous ammonia converts it into a substance deposited in black needles. Aniline gave the same products with it as with the tetrachlororthoquinone which are described later in this paper.

*Hexachlororthodihydroxypyrocatechin Ether*, $C_6Cl_4O_2.C_6Cl_2(OH)_2$.—Ten grams of the hexachlororthoquinopyrocatechin ether were reduced with 3 per cent sodium amalgam and water in a flask kept full of carbonic dioxide. After the reaction had run at ordinary temperatures for several days, the red quino ether had been converted into a white product, which, however, turned purple on exposure to the air. The dark colored alkaline filtrate gave marked tests for a pyrocatechin. The solid product was purified by washing successively with dilute hydrochloric acid and alcohol, and then crystallizing it from a mixture of equal parts of benzene and alcohol, till it showed the constant melting point of 290°, when it was dried at 100° for analysis:

I. 0.1986 gram substance gave 0.4019 gram AgCl.
II. 0.0590 gram substance gave 0.1211 gram AgCl.

| | Calculated for $C_6Cl_4O_2.C_6Cl_2(OH)_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Cl | 50.36 | 50.03 | 50.74 |

*Properties of Hexachlororthodihydroxypyrocatechin Ether.*—It crystallizes in needles which differ in color according to the solvent used; from alcohol they are white, from a mixture of equal parts of alcohol and benzene a delicate heliotrope-purple, from nitrobenzene chocolate-brown. It melts at 290°, that is, at a decidedly lower temperature than the corresponding bromine compound; and is also distinctly more soluble than that, although only slightly soluble in all the common organic solvents except nitrobenzene. The best solvent for it is a mixture of equal parts of alcohol and benzene. Fuming nitric acid converts it quantitatively into the red hexachlororthoquinopyrocatechin ether. Sodic hydrate has a very slight solvent effect, but turns the undissolved crystals deeper purple.

*Action of Aniline on Tetrachlororthoquinone.*[1]—Five grams of tetrachlororthoquinone, dissolved in 100 cc. of alcohol, were added, in small portions at a time, to a cold solution of 7.5 grams of aniline in 100 cc. of alcohol, the mixture being thoroughly stirred after each addition. Under these conditions a voluminous, light brown precipitate of anilinedianilinodichlororthoquinone was formed, which was filtered out, after half the solution of quinone had been added. The remaining half of the solution of quinone was then added to the red filtrate, and stirred vigorously. At first a thick, dark greenish mass was formed, but, as the stirring continued, the color became lighter until the solid was changed into small, glistening, yellow flakes of the ethyl alcohol-dianilinodichlororthoquinone, which were also filtered out. This second filtrate was allowed to stand for several hours, or warmed for a short time, when it deposited black crystals of dianilinochlorparaquinoneanil, or it was boiled under a return condenser for 3 or 4 days, which formed the dark brown needles of dianilinoparaquinoneanil. The same

[1] Jackson and Porter: THIS JOURNAL, 30, 518 (1903).

change took place with the bromine compound by boiling for only 2 to 4 hours.

*Dianilinodichlororthobenzoquinone*, $C_6Cl_2(C_6H_5NH)_2O_2$.—This substance was not a direct product of the action of tetrachlororthoquinone on aniline, but was obtained from the bulky brown precipitate of its aniline compound made as described above. For this purpose it was dried in the air and then heated with a mixture of 5 parts of benzene and 1 of ligroin, which changed its color to reddish purple in a few minutes. The undissolved purple crystals were filtered out, and treated 3 times in the same way, with fresh portions of the mixture of 5 parts of benzene and 1 of ligroin. Finally, it was purified by crystallization from a large amount of this same mixture, until it showed the constant melting point 194°–195°, when it was dried for analysis. The decomposition of the aniline compound, $C_6Cl_2(C_6H_5NH)_2O_2.C_6H_5NH_2$, was brought about apparently by the slight solubility of the dianilino body and the easy solubility of the aniline in the mixture of benzene and ligroin; it is, therefore, necessary to repeat the treatment several times with fresh portions of the mixture to insure complete decomposition. The filtrates contained aniline and a little of the brown aniline compound.

0.1891 gram of substance gave 0.1491 gram AgCl.

| | Calculated for $C_6Cl_2(C_6H_5NH)_2O_2$. | Found. |
|---|---|---|
| Cl | 19.77 | 19.49 |

*Properties of Dianilinodichlororthoquinone.*—It crystallizes from a mixture of benzene and ligroin in reddish purple, tapering needles, which melt at 194°–195°. It is easily soluble in benzene, slightly soluble in ligroin. The best solvent for it is the mixture of 5 parts of benzene with 1 of ligroin. Strong hydrochloric acid acts on it slightly; strong nitric acid dissolves it with decomposition; strong sulphuric acid gives a greenish solution with it; sodic hydrate dissolves it with decomposition. It was easily reduced with zinc dust and acetic acid to a substance which gave tests for a pyrocatechin, but was not further studied. Its most characteristic property is its strong tendency

to form addition compounds. Those with aniline and with ethyl alcohol are described below.

*Aniline Dianilinodichlororthobenzoquinone,* $C_6Cl_2(C_6H_5NH)_2O_2.C_6H_5NH_2$.—This substance was the light brown precipitate obtained as the first product of the reaction of tetrachlororthoquinone with aniline, in alcoholic solution. It was also made by boiling a benzene solution of the dianilinodichlororthoquinone with the calculated quantity of aniline. In either case the substance was purified by recrystallization from benzene, until it showed the melting point 164°–165°, when it was dried *in vacuo* for analysis. It seems strange that this substance should crystallize unaltered from benzene, when it is decomposed by solution in a mixture of 5 parts of benzene and 1 of ligroin. An attempt has been made to explain this phenomenon in the introduction.

I. 0.1413 gram substance gave 0.0930 gram AgCl.
II. 0.1864 gram substance gave 0.1234 gram AgCl.

| | Calculated for $C_6Cl_2(C_6H_5NH)_2O_2.C_6H_5NH_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Cl | 15.71 | 16.28 | 16.37 |

*Properties of Aniline Dianilinodichlororthoquinone.*—It crystallizes from boiling benzene in long, fine, light brown needles, which melt, with decomposition, at 164°–165°. It is soluble to a certain extent in all the common organic solvents, from some of which, like benzene, it is deposited unaltered, while from others the dianilinodichlororthoquinone separates, and aniline is left in solution. This decomposition seems to be produced by solvents in which the dianilino body is but slightly soluble. A mixture of benzene and ligroin shows this reaction excellently. The free aniline was identified in the benzene-ligroin mother liquor by the formation of a soluble hydrochloride with hydrochloric acid, and the phenylisonitrile test. Strong hydrochloric or nitric acid dissolves and decomposes it, strong sulphuric acid forms with it a green solution; sodic hydrate, in hot aqueous solution, decomposes it.

*Ethyl Alcohol Dianilinodichlororthobenzoquinone,* $C_6Cl_2(C_6H_5NH)_2O_2.C_2H_5OH$.—This substance is the yellow product formed by the action of tetrachlororthoquinone on

aniline, as described above. It was also prepared by allowing dianilinodichlororthoquinone, or its addition compound with aniline to stand for several days in contact with cold alcohol. In either case it was purified by crystallization from warm alcohol, until it showed the constant melting point 140°–141°, when it was dried *in vacuo* for analysis:

0.1032 gram substance gave 0.0734 gram AgCl.

| | Calculated for $C_4Cl_2(C_6H_5NH)_2O_2.C_2H_5OH$. | Found. |
|---|---|---|
| Cl | 17.53 | 17.58 |

*Properties of Ethyl Alcohol Dianilinodichlororthoquinone.*—It crystallizes from warm alcohol in plates of a chrome yellow color, which melt, with decomposition, at 140°–141°. It dissolves easily in alcohol, ether, benzene, toluene, or acetone; very slightly soluble in ligroin. A boiling mixture of 5 parts of benzene and 1 of ligroin decomposes it with the formation of the dianilinodichlororthoquinone. It is easily soluble in the strong mineral acids, or in sodic hydrate.

*Dianilinochlorparaquinoneanil,* $C_6HCl(C_6H_5NH)_2ONC_6H_5$.—This substance was the third product of the action of tetrachlororthoquinone on an alcoholic solution of aniline. It is more stable than the 3 compounds just described; and was also prepared by boiling any one of these with an alcoholic solution of aniline, but the boiling must not be too long continued, as in that case some dianilinoparaquinoneanil will be formed. The black shining crystals, prepared by any of these methods, were purified by crystallization from a mixture of equal parts of benzene and methyl alcohol, until they showed the constant melting point 180°, when they were dried for analysis:

0.1368 gram substance gave 0.0484 gram AgCl.

| | Calculated for $C_6HCl(C_6H_5NH)_2ONC_6H_5$. | Found. |
|---|---|---|
| Cl | 8.88 | 8.75 |

*Properties of Dianilinochlorparaquinoneanil.*—It crystallizes from a mixture of benzene and methyl alcohol in brilliant black, flattened, blunt needles, which melt at 180°. It is easily soluble in benzene, toluene, acetone, ethyl acetate, or glacial

acetic acid; less soluble in ethyl or methyl alcohol, or in ether; slightly soluble in ligroin. The best solvent for it is a mixture of equal parts of benzene and methyl alcohol. It dissolves in hot strong hydrochloric acid with a green color; strong nitric acid dissolves it with decomposition; strong sulphuric acid dissolves it with a dark purple color. This indicates that the substance does not belong to the ortho series as the ortho-quinones described above gave a green color with sulphuric acid. A strong solution of potassic hydrate has no apparent effect on it whether hot or cold. The reasons for believing it to belong to the para series, in addition to the color reaction with sulphuric acid already mentioned, are that it shows no tendency to form addition compounds, a specimen undergoing no change even after standing with methyl alcohol for 2 weeks, and its easy conversion into the known dianilinoparaquinoneanil, which was brought about by treating its ethereal solution with sulphurous dioxide. The same change was produced by boiling the substance with aniline and alcohol for 3 to 4 days, but this last observation is of no use in determining its constitution, as during this long action an ortho derivative might well have passed over into the para series.

*Dianilinoparaquinoneanil*, $C_6H_2(C_6H_5NH)_2ONC_6H_5$. — This substance was obtained by boiling for 3–4 days, under a reverse condenser, the last filtrates formed in working up the products of the action of tetrachlororthoquinone on aniline dissolved in alcohol, or boiling any of the dianilino compounds just described with aniline and alcohol, or by treating an ethereal solution of dianilinochlorparaquinoneanil with sulphurous anhydride. To purify the product it was washed with cold ethyl alcohol and then recrystallized from a mixture of benzene and methyl alcohol. This substance was discovered by Zincke and Hagen,[1] who made it by the action of aniline, dissolved in acetic acid, on paraquinone. They give the melting point as 202°–203°, but, as was also observed by Porter and one of us,[2] it is a very difficult matter to raise the melting point beyond about 198°. Accordingly, we identified it by

[1] Ber. d. chem. Ges., 18, 785 (1885).
[2] This Journal, 30, 534 (1903).

comparing our specimen with one made by Porter from paraquinone by Zincke and Hagen's method and one made by him from tetrabromorthoquinone. All three of these specimens were recrystallized from a mixture of equal parts of benzene and methyl alcohol, when they all showed the same color and characteristic comb-like crystals, the melting point 198°, and the same color reactions, blue with strong hydrochloric acid, brown with nitric acid, and reddish brown with strong sulphuric acid. There can be no doubt, therefore, of the identity of our product.

*Pentachlordiketotetrahydrobenzene*, $C_6HCl_5O_2$?—When an excess of chlorine was added to the acetic acid filtrates from the preparation of tetrachlorpyrocatechin, the liquid turned red, and after standing for 7 months deposited long, brass-colored needles, which were recrystallized from glacial acetic acid and dried at 100° for analysis.

0.1540 gram substance gave 0.3927 gram AgCl.

| | Calculated for $C_6HCl_5O_2$. | Found. |
|---|---|---|
| Cl | 62.84 | 63.06 |

As we made only this single analysis of the substance, its nature cannot be considered settled, but in accordance with this result it may be called, provisionally, pentachlordiketotetrahydrobenzene.

*Properties.*—It crystallizes from glacial acetic acid in brassy yellow, hexagonal plates with a brilliant luster, which melt at 146°–147° to a brown liquid. It is hoped that the investigation of this substance can be taken up in this laboratory in the near future.

Work on the action of benzaldehyde, or acetone on tetrachlororthoquinone, is described in the introduction to this paper.

CAMBRIDGE, MASS.,
Aug. 3, 1906.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

# ON ALDOL, PENTAERYTHROSE AND THE ACTION OF COPPER ACETATE ON THE HEXOSES.

By A. F. McLeod.

All the condensation reactions shown by aldehydes in the presence of alkalies have been classified by Nef[1] under the head of olefine and alkylidene condensations.

It is now possible, in the light of Nef's work on aldehydes, alcohols, etc., during the past 12 years[2] and because of some observations of my own on acetaldehyde which were made at Dr. Nef's suggestion and under his guidance, to formulate these reactions more precisely. An aqueous solution of an aldehyde contains the following substances in dynamic equilibrium:

$$RHC:O + H_2O \rightleftarrows RHC(OH)_2 \rightleftarrows RCOH + H_2O.$$

Aldehyde. Alkylidene dihydroxide. Hydroxyalkylidene.

$$[R = C_nH_{2n+1}, C_6H_5 \text{ or } H.]$$

Now it is well known that an aldehyde, in aqueous solution, never goes over into its condensation products at temperatures between 20° and 100°; polymerization of the active aldehyde molecules,

$$3RHC(-O-) \rightleftarrows (RHC(-O-))_3,$$

on the other hand, may often take place spontaneously.

When we treat an aldehyde with an aqueous solution containing an alkali or an alkaline salt, *e. g.*, caustic or mild alkalies, potassium cyanide, sodium or potassium formate or acetate, etc., condensation often takes place at once in the cold even in the presence of a marvelously small amount of the reagents named. What is the function of the alkali in these cases and how may its concentration affect the end result? The aldehydes in the form of their hydrates are $RHC(OH)_2$, the alkylidene dihydroxides are really diatomic alcohols; they must, there-

[1] Ann. Chem. (Liebig), **298**, 219–223.

[2] *Ibid.*, **298**, 202–374; **309**, 126–189; **310**, 316–335; **318**, 1–57, 137–230; **335**, 191–333.

fore, possess, like all alcohols, weak acid properties and be capable of salt formation;[1] and the exhaustive experiments of Nef on the monatomic as well as on the polyatomic alcohols have shown conclusively that the salts of all primary and secondary alcohols are relatively much more dissociated into alkylidene,

$$RR'CHOM \rightleftarrows RR'C< + HOM,$$

than the corresponding free alcohols. It is, therefore, self-evident that an aldehyde in the presence of an alkaline salt, or even of powdered calcium carbonate at 100°,[2] must be *relatively more* dissociated into hydroxyalkylidene,

$$R(HO)CHOM \rightleftarrows R(HO)C< + HOM.$$

As soon as the concentration of the hydroxyalkylidene reaches a certain definite limit, a condensation reaction, or a decomposition of the water present by the hydroxyalkylidene must take place. Often both reactions occur simultaneously.

Thus, according to unpublished observations of Nef, when 4 liters of 1 per cent aqueous formaldehyde are treated, in the cold, with 24 grams of powdered quicklime, 80 per cent of the reaction proceeds slowly according to

$$\text{(I)}\quad CH_2O + (HO)CH< + 2HO{-}H \rightarrow HOCH(OH)_2 + 2H{-} + CH_2{-}O \rightarrow \begin{matrix} H & OH \\ C & \\ & O \end{matrix} + H_2O + CH_3OH,$$

and only 20 per cent according to

$$\text{II.}\quad 6HOCH< \rightarrow 3\ \begin{matrix} HOCH \\ \vdots\vdots \\ HOCH \end{matrix} \rightarrow 3HOCH_2CH:O \rightarrow C_6H_{12}O_6.$$

If, on the other hand, small amounts of lead hydroxide,[3] or powdered calcium carbonate[4] be used in place of lime, then re-

[1] Nef: Ann. Chem. (Liebig), **318**, 138–187; **335**, 312. Cf. Euler: Ber. d. chem. Ges., **39**, 36–45.

[2] Euler: Ber. d. chem. Ges., **39**, 45.

[3] Lobry de Bruyn and Ekenstein: Rec. Trav. Chim., **18**, 309.

[4] Euler: Ber. d. chem. Ges., **39**, 45.

action II., *i. e.*, sugar formation, is the chief reaction. The remarkable difference in the result is obviously simply due to the fact that the concentration of hydroxymethylene, present in Lobry de Bruyn's and in Euler's experiments, is *far smaller* than when lime, or some other caustic alkali is used; consequently polymerization of 2 hydroxymethylene molecules to dihydroxyethylene which then goes over spontaneously into glycolyl aldehyde, etc., is the chief reaction in the former case. Similarly 2 molecules of hydroxyphenylmethylene, $C_6H_5\overset{\wedge}{C}OH$, formed from benzylidenedihydroxide by dissociation, polymerize[1] to dihydroxystilbene, $\begin{matrix} C_6H_5COH \\ \vdots\vdots \\ C_6H_5COH \end{matrix}$, which then spontaneously transforms itself, probably, without an intermediate addition of water, into benzoin, $C_6H_5C : OCH(OH)C_6H_5$. In the case of benzaldehyde the benzoin condensation (*i. e.*, reaction II.) is possible only by using small amounts of potassium cyanide, which here obviously serves a double purpose, first in increasing the amount of methylene dissociation and second in uniting temporarily with the hydroxyphenylmethylene to form an easily dissociable double salt, $C_6H_5(HO)C:CNK$, analogous to the double cyanides and fulminates.[2] When, on the other hand, benzaldehyde is treated with cold, concentrated, aqueous potassium hydroxide, molecular amounts of benzyl alcohol and benzoic acid are formed according to reaction I. It should be *especially emphasized* that only *tertiary* aldehydes, such as benzaldehyde, trimethylacetaldehyde, $(CH_3)_3 : CCH:O$, etc., *i. e.*, those which contain the aldehyde group bound to a carbon atom which is free from hydrogen can undergo the benzoin condensation—which is simply due to a polymerization of two hydroxyalkylidene molecules,

$$2\overset{\wedge}{RCOH} \rightleftharpoons \begin{matrix} RCOH \\ \vdots\vdots \\ RCOH \end{matrix},$$

etc. The conversion of formaldehyde into glycollic aldehyde

[1] Nef: Ann. Chem. (Liebig), 298, 312.

[2] Nef: *Ibid.*, 280, 334-338; 298, 313. Cf. Goldthwaite: THIS JOURNAL, 30, 466, foot-note.

must, however, also be considered as a benzoin condensation. Why is it that the ordinary aliphatic aldehydes do not undergo an analogous benzoin condensation on treatment with alkaline reagents? The reason for the well-known difference in behavior is easily understood on the basis of the following considerations which have been presented for some years past by Dr. Nef in his lectures on organic chemistry, and which are simply an application of his ideas on the laws of condensation presented in a paper of his.[1] A primary or a secondary aldehyde, $RCH_2CH:O$ and $(RR')CHCH:O$, still contains on the carbon atom holding the CHO group one or more easily dissociable non-ionic hydrogen atoms.

When, therefore, the concentration of the hydroxyalkylidine molecules is in these cases increased by the addition of a mild or caustic alkali, or an alkaline salt, the following 2 entirely independent reactions may take place simultaneously or singly:

(I.) Decomposition of the water, or caustic alkali present by the hydroxyalkylidene according to

$$RR'CH{-}\underset{|}{CH}{-}\underset{|}{O} + RR'CH{-}\overset{\diagup\diagdown}{C}(OH) + 2H{-}OH \rightarrow RR'CHCH_2OH + RR'CHC(OH)_3.$$

Reaction I. is, therefore, common to all aldehydes, whether primary, secondary or tertiary; the Dumas-Stas reaction, whereby all aldehydes are converted quantitatively by potash-lime at 200°–250°, into hydrogen and the potassium salt of the corresponding fatty acid,

$$RCH:O + KOH \rightarrow RCOOK + H_2,$$

is obviously simply a special phase of reaction I.

(II.) The hydroxyalkylidene may transform itself, by intramolecular addition,[2]

$$RR'\overset{\diagup\diagdown}{CHCOH} \rightarrow RR'\underset{||}{C}CHOH \rightarrow RR'C:CH(OH),$$

into an olefine derivative, which then at once unites with the unchanged aldehyde present, according to

[1] Ann. Chem. (Liebig), 298, 202-374.
[2] Nef: *Ibid.*, 318, 1–57; 335, 196–200.

$$RR'CCH(OH) + H{-}CRR'CHO \rightleftharpoons (RR')CHCH(OH)CRR'CH{:}O,$$

giving an aldol (olefine condensation). The aldols thus formed may then give in many cases, by further loss of water, olefine derivatives, *e. g.*, acetaldol goes over, in the presence of traces of alkali or acid, with remarkable ease, by loss of water, into crotonaldehyde, in 2 stages, see below. A polymerization of 2 hydroxyalkylidene molecules,

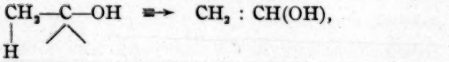
$$(RR')CHCOH,$$

to a benzoin-like body,

$$RR'CHC(OH){:}C(OH)CHRR' \rightleftharpoons RR'CHCOCH(OH)CHRR',$$

which is also possible from a theoretical standpoint in the case of primary and secondary aldehydes has, up to the present time, never been observed; such a transformation is, indeed, highly improbable because of the ease with which the intramolecular addition reaction II., just cited, must take place as soon as the concentration of the hydroxyalkylidene present is above a definite limit. It is, however, not impossible that in the future certain primary and secondary aldehydes may be found which, in addition to the ordinary aldol condensation, may also undergo a benzoin condensation.

In studying the action of caustic alkalies and alkaline carbonates on acetaldehyde I have, moreover, made the following important observation: When the concentration of alkali used is below a certain definite limit, which is 0.1 per cent in the case of sodium and calcium hydroxides, no appreciable condensation of the acetaldehyde to aldol or crotonaldehyde takes place, even after weeks of standing at ordinary temperatures. This is just what one would expect from the theory presented above, a certain definite amount of alkali is obviously necessary in order to increase the concentration of the hydroxyethylidene molecules in quantity sufficient to enable the transformation into vinyl alcohol,



to take place, and this is a condition *sine qua non* in Nef's theory of aldol condensation. Nef has shown, furthermore, that when freshly precipitated oxide of mercury is present the vinyl alcohol first set free by the addition of alkalies is prevented from uniting with unchanged aldehyde to give aldol because it unites *by preference* with the metallic oxide introduced into the system[1] to form an insoluble white salt, which readily gives back acetaldehyde on treatment with dilute acids.

Finally, it is well known from Lieben's experiments that when molecular mixtures of various aliphatic aldehydes are treated with alkalies, only one of the two theoretically possible mixed aldols is formed; thus acetaldehyde gives, with isobutyric aldehyde, only

(I.) $CH_3CH(OH)C(CH_3)_2CH : O$,

and not a trace of

(II.) $(CH_3)_2CHCH(OH)CH_2CH : O$.

This can only be due to the fact that acetaldehyde is converted into vinyl alcohol far more readily and with much smaller concentration of the alkali than is isobutyric aldehyde into the corresponding vinyl alcohol homologue, $(CH_3)_2 : CCH(OH)$; consequently, vinyl alcohol absorbs isobutyric aldehyde to give product I.

The fact that remarkably different minimal concentrations of alkali are required in the case of the various aldehydes in order that a transformation according to II., *i.e.*, a benzoin or aldol condensation may take place, is of the utmost importance in synthetic work. Thus it is clear that when aqueous mixtures of acetaldehyde and formaldehyde are treated with potassium or sodium hydroxides, taking care to keep the concentration of the alkali used below 0.1 per cent, no trace of aldol or crotonaldehyde can be formed; the formaldehyde, on the other hand, which is by far the most sensitive of all the aldehydes towards alkalies and is even condensed in the presence of calcium carbonate to

[1] Ann. Chem. (Liebig), **298**, 316–318.

hexoses, must contain, under the conditions named, a sufficiently large concentration of hydroxymethylene molecules to form at once with the acetaldehyde present a mixed aldol. Tollens[1] has, in fact, shown that one can obtain large amounts of pentaerythrite, $C(CH_2OH)_4$, from aqueous solutions of acetaldehyde and formaldehyde (4 mols.) in the presence of calcium hydroxide. It is evident, from Nef's work, that this reaction proceeds through the following 5 successive stages:

$$3HOCH< + H—CH_2CHO \rightarrow$$

Hydroxymethylene (*a*).

$$HOCH_2CHHCHO + HOCH< \rightarrow$$

Hydracrylic aldehyde (*b*).

$$(HOCH_2)_2CHCHO + >CHOH \rightarrow (HOCH_2)_3CCHO$$

$\beta\beta'$-Dihydroxyisobutyric aldehyde (*c*). Pentaerythrose (*d*).

$$(CH_2OH)_3 : CCHO + >CHOH + 2H—OH \rightarrow$$

$$(HO)_2CHOH + (CH_2OH)_3 : CCH_2OH.$$

Pentaerythrite (*e*).

I have consequently taken up, at Dr. Nef's wish, a renewed study of the action of alkalies on mixtures of acetaldehyde and formaldehyde with the object of proving, by experiment, that the reaction takes place through the stages indicated; it was *a priori* improbable that an intermediate formation of hydracrylic aldehyde (*b*), or even of $\beta\beta'$-dihydroxyisobutyric aldehyde (*c*) could be proved by direct means, since the non-ionic $\alpha$-hydrogen atoms still left bound to the carbon atom containing the CH:O group in these intermediate products must be *relatively* far more dissociated from carbon than the corresponding ones in acetaldehyde; consequently these substances must, in the main, be at once absorbed by more hydroxymethylene to give pentaerythrose (*d*).

I succeeded, therefore, in obtaining large amounts of pentaerythrose in the reaction under discussion; and the indications point also to the presence of relatively large amounts of $\beta\beta'$-dihydroxyisobutyric aldehyde (*c*) in the crude material obtained. That the reaction proceeds through stage (*b*) was, furthermore,

[1] Ann. Chem. (Liebig), **265**, 316; **276**, 58.

definitely established because mixtures of hydracrylic aldehyde, which has recently been discovered by Nef, and of formaldehyde (2 mols.) give, when treated with traces of sodium hydroxide, an almost quantitative yield of crude pentaerythrose.

## EXPERIMENTAL PART.

It is clear from a study of the literature on the subject that acetaldehyde, when treated with mild or caustic alkalies, or with concentrated sulphuric acid, is transformed successively into aldol, crotonaldehyde, oily volatile and non-volatile condensation products of crotonaldehyde and, finally, into aldehyde resin; the constitution, or even the homogeneous character of the 3 last-named products, has not yet been ascertained.

The following experiments with acetaldehyde prove that when the concentration of the mild or caustic alkali used is below a certain definite limit, no condensation of the acetaldehyde takes place even on 6 weeks' standing at ordinary temperatures; furthermore, the conditions under which the best yield of aldol and of crotonaldehyde can be obtained from acetaldehyde were thoroughly investigated. It was definitely established that aldol, as well as crotonaldehyde, never gives back a trace of acetaldehyde on treatment with water, with very dilute alkalies, or with acids in sealed tubes at 100°. Aldol goes over, under these conditions with the greatest ease, into crotonaldehyde, which is, in turn, converted into insoluble, yellow, volatile and non-volatile oils and, finally, into aldehyde resin.

### *Manufacture of Acetaldehyde and Its Behavior towards Dilute Alkalies.*

Since preparations of acetaldehyde invariably contain a greater or less proportion of paraldehyde, all the acetaldehyde used in my experiments was prepared from paraldehyde by dissociation. A few drops of concentrated sulphuric acid have been usually used for this purpose, but there is always considerable loss through charring by this process. The following method is thoroughly reliable and always gives at least a 90 per cent yield. Paraldehyde, 212.2 grams, and 20 per cent sulphuric acid, 10 cc., are mixed and heated in a flask provided

with a Glinsky apparatus. The temperature of the surrounding bath is kept at 85°–95°, whereupon acetaldehyde rapidly distils over; on redistillation, 190.4 grams of aldehyde, b. p. 21°–27°, were regularly obtained. Ten grams of aldehyde were dissolved in the cold in 10 cc. of saturated lime water, proved by titration with standard acid to contain 0.01617 gram of calcium hydroxide; the mixture was then allowed to stand at room temperature for 6 weeks. On heating the alkaline solution on a boiling water-bath and subsequently drying the distillate with calcium chloride, 8.4 cc. of aldehyde, b. p. 21°–30°, were recovered unchanged. This is 67.2 per cent of the amount originally taken.

A second experiment, in which 10 grams of aldehyde and 10 cc. of 0.1 per cent sodium hydroxide, containing, as determined by titration with standard acid, 0.01154 gram of sodium hydroxide, were used, gave the following result: After standing for 21 days at room temperature no trace of coloration or of formation of insoluble aldehyde resin could be observed. The alkaline solution was now heated on a boiling water-bath to drive off the unchanged aldehyde, proceeding as in the first experiment. Seven and eight-tenths cc. of aldehyde, b. p. 21°–30°, were recovered. Furthermore, titration of the aqueous alkaline solution, left after distilling off the aldehyde, with standard acid proved that 0.0112 gram of sodium hydroxide was still present, only 0.3 milligram, therefore, had been used up. These experiments prove that when the concentration of the calcium or sodium hydroxide solutions is 0.1 per cent no condensation or only exceedingly slow condensation of acetaldehyde takes place. It is very probable that 0.2 per cent sodium or potassium carbonate solutions will have no condensation effect on aldehyde. I expect, moreover, to continue experiments in this direction at once, in the autumn, including also a study of the action of such substances as potassium cyanide, sodium and potassium acetate, etc.

*Manufacture of Aldol and of Crotonaldehyde, and Behavior of These Substances towards Water, Dilute Alkalies and Acids, Etc.*

The only 2 satisfactory methods of preparing aldol in quan-

tity are those of Halpern[1] and of Orndorff and Newbury[2] from acetaldehyde and small amounts of powdered potassium carbonate, or 10 per cent aqueous potassium carbonate, respectively. In both cases the yield of pure distilled aldol obtained was never over 50 per cent of that demanded by theory. I have always obtained a large and practically constant yield, 60 per cent, of aldol by the following method, which is essentially that of Orndorff and Newbury.

A solution of 47 grams of aldehyde in 20 grams of water was treated, in the cold, with 2 grams of potassium carbonate, dissolved in the smallest possible amount of water. The temperature was kept below 10° for the first half hour and the mixture was then left standing, at ordinary temperatures, for 18 hours. The aldol was removed from the aqueous solution by extracting 3 times with ether. After drying with calcium chloride, and removing the last traces of ether by heating in a flask, up to 80° (20 mm.), 41 grams of crude, yellowish aldol were obtained. This gave, on distillation, 28.3 grams of the pure product boiling at 79° (20 mm.) and only 5.1 grams of higher boiling oil remained in the distilling flask. Considerable loss, 15–20 per cent, must, therefore, have occurred through volatilization. Two further experiments, carried out in practically the same manner, and with the same amount of material, gave, after 1 distillation, 48–50 per cent of pure aldol and 20–35 per cent of higher boiling oils.

Another experiment with 20 grams of aldehyde, 8 grams of water and 1 gram of potassium carbonate gave, after 18 hours' standing, by acidifying with the calculated amount of hydrochloric acid and then heating on a boiling water-bath, 3 cc. of aldehyde, boiling at 21°–35°; this proves that about 12 per cent of the aldehyde is left unchanged in the process used. Nevertheless, it is not advisable to allow the alkaline solutions to stand longer than 18 hours, to insure complete transformation of the aldehyde, because aldol itself is rapidly acted upon under the conditions employed, as was also proved by special experiments. Thus it was observed that when the alkaline solu-

[1] Monats. Chem., **13**, 517.
[2] *Ibid.*, **22**, 59.

tion stood longer, 48 hours for example, instead of 18, only 20–30 per cent, or even less, of pure aldol was obtained and the amount of non-volatile and higher-boiling yellowish oil was correspondingly increased. Special experiments have also shown that it is impossible to obtain aldol in appreciable quantity from aldehyde either by means of traces of powdered potassium hydroxide or by using aqueous solutions of this substance in concentration varying from 0.1 per cent to 2 per cent.

In order, finally, to obtain crotonaldehyde in quantity for investigation it was found, after repeated trial of various methods given in the literature, that the following process gives by far the best yield: Crude aldol, made from aldehyde and 10 per cent potassium carbonate, as stated above, is mixed with 0.5 of its weight of powdered potassium bisulphate and heated rapidly first at 120°–130° and finally in a bath at 180°–200.° The distillate, after separating from small amounts of water and drying with calcium chloride, boils at once at 98°–106°. The yield was found to be regularly 70–73 per cent of that demanded by theory.

My experience with Lieben's method[1] for making crotonaldehyde was as follows: A mixture of 15 cc. of acetaldehyde and 5 cc. of 28 per cent sodium acetate was heated for 10 hours, in a sealed tube, at 100°. On working up by heating first in a bath at 100° and then at 120°–130°, etc., 9 cc. of acetaldehyde, 2.4 cc. of crotonaldehyde, boiling at 98°–106° and 1.2 grams of yellow, mobile oil, boiling at 90°–120° (24 mm.) were obtained. Similar mixtures of aldehyde and sodium acetate, when heated longer at 100°, *e. g.*, for 36 hours, gave only small amounts of unchanged aldehyde and of crotonaldehyde. The main product was an insoluble, reddish, mobile oil which, on fractionation (20 mm.), boils in part at 90°–120° and leaves much non-volatile, viscous, red gum—obviously condensation or polymerization products of crotonaldehyde. Finally, Orndorff and Newbury's method of making crotonaldehyde,[2] by direct heating of aldol under ordinary pressures, gave, under the most

[1] Monats. Chem., 13, 519.

[2] *Ibid.*, 13, 517.

favorable conditions, only a 37.5 per cent yield of the product. Thus 13.5 grams of aldol, boiling at 79° (20 mm.), when heated in a flask connected with a Glinsky apparatus, a condenser, and well-cooled receiver, gave, finally, after heating in a bath from 190°–220°, 0.4 gram of aldehyde, boiling at 21°–30°, 4 grams of crotonaldehyde, boiling at 102°–106°, and 4 grams of much higher boiling yellow oil remained in the distilling flask. Furthermore, 11 grams of aldol, heated for 6 hours in a sealed tube at 180°–200°, gave an entirely similar result. An exceedingly good method for making crotonaldehyde is simply to heat aldol with 12 parts of water for 14 hours, in a sealed tube, at 100°; a 73 per cent yield is regularly obtained. No trace of aldehyde, but small amounts of yellow crotonaldehyde condensation products are also formed in this case. The separation of crotonaldehyde from water involves on difficulty, as on distillation of an aqueous solution the aldehyde comes over entirely with small amounts of water in the first portion of the distillate. The first fraction is, therefore, simply redistilled, or is often freed at once from small amounts of water by drying with calcium chloride, etc.

A solution of 6.4 grams of crotonaldehyde, b. p. 103°–104°, in 70 cc. of water, was heated in a sealed tube, at 100°, for 43 hours, with the following result: Three cc. of dry crotonaldehyde, boiling at 98°–103°, were recovered unchanged. On extracting the aqueous solution with ether, etc., only 0.5 gram of yellowish oil was obtained, one-half of which boiled from 84°–86° (29 mm.) and the remainder was non-volatile. It is possible that the small amount of volatile oil obtained was aldol but, unfortunately, we have no means of sharply identifying aldol by conversion into a crystalline derivative. In any case, the results obtained show that the behavior of aldol and crotonaldehyde towards water is in marked contrast to that of the lower homologues, hydracrylic aldehyde and acrolein.[1]

The following experiment made with crotonaldehyde and 0.1 per cent sodium hydroxide proves that it is slowly converted, at ordinary temperatures, into high-boiling and non-volatile red oils. Since acetaldehyde remains practically un-

[1] Ann. Chem. (Liebig), 335, 219.

changed on similar treatment and aldol is converted very rapidly under these conditions, first into crotonaldehyde, etc., it is obviously impossible, by means of caustic alkalies, to convert aldehyde either into aldol or crotonaldehyde, as was also shown by special experiments described above.

In the first place it was proved that a mixture of 3.5 grams of crotonaldehyde and 3.5 grams of 0.1 per cent sodium hydroxide, when distilled directly, give back 2.7 grams of dry crotonaldehyde boiling at 98°–106°; in addition, 0.3 gram of non-volatile, insoluble, red oil was obtained.

Five and three-tenths cc. of crotonaldehyde were now dissolved in 30 cc. of cold 0.1 per cent sodium hydroxide and the mixture was then allowed to stand in a closed vessel for 14 days at ordinary temperatures. On distillation 2.2 cc. of unchanged crotonaldehyde, which is 42 per cent of the amount taken, were recovered; in addition 0.3 gram of thick red oil, boiling at 90°–120° (30 mm.), and 1.3 grams of brown, non-volatile resin were obtained from the alkaline solution by extraction with ether, etc.

On mixing equal volumes of aldol and 1 per cent sodium hydroxide in the cold, a noticeable rise of temperature is observed; the solution turns yellow, the odor of crotonaldehyde is very perceptible and soon an insoluble, yellowish oil separates out which gradually sinks and is transformed into a thick red oil. This oil, which is insoluble in water and freely soluble in ether, remains non-volatile when heated in a bath at 300° (20 mm.). Crotonaldehyde, on similar treatment, gives, apparently, the same red oil, which is obviously an intermediate product in the transformation of aldehyde, aldol, crotonaldehyde, etc., by caustic alkalies or concentrated sulphuric acid into aldehyde resin. The following experiments with aldol also show how readily this substance goes over into crotonaldehyde. A mixture of 6.4 grams of aldol, 14 cc. of water and 2 cc. of 0.1 per cent sodium hydroxide gave, after heating in a sealed tube at 100°, for 12 hours, no trace of acetaldehyde but 3.5 cc. of crotonaldehyde, or 71 per cent of the theory, and a total of 1.5 grams of high-boiling as well as non-volatile red oils.

Thirteen and three-tenths grams of aldol, b. p. 79° (20 mm.), and 50 cc. of water containing 1 gram of crystallized sodium acetate were heated in a sealed tube, for 20 hours, at 100°; no trace of acetaldehyde was formed, but 2.6 cc. of crotonaldehyde, boiling at 98°–106°, were obtained. The alkaline solution gave, on extracting with ether, etc., 5.8 grams of reddish oil which, on distillation (30 mm.), decomposed to a large extent, giving 1 cc. of yellowish, mobile oil, boiling at 100°–150° and leaving 1.6 grams of non-volatile red gum in the distilling flask.

A similar experiment, in which 13.9 grams of crotonaldehyde and 5 cc. of 28 per cent sodium acetate solution were heated in a sealed tube for 20 hours, at 100°, gave no trace of acetaldehyde but 6.4 cc. of unchanged crotonaldehyde and 4 grams of non-volatile reddish gum.

Six and five-tenths grams of aldol were dissolved, in the cold, in 70 cc. of water containing 0.5 gram of potassium carbonate. The solution became yellow and smelt strongly of crotonaldehyde. On working up in the usual manner, after 2 days' standing at ordinary temperatures, only a very small amount of crotonaldehyde and no trace of acetaldehyde was formed. The main product was a reddish, non-volatile gum, insoluble in water—obviously a condensation or polymerization product of crotonaldehyde.

A solution of 9.7 grams of aldol in 10 cc. of 1 per cent sulphuric acid was heated for 5 hours in a sealed tube, at 100°; 5.3 grams of thick brown oil had separated from the aqueous layer and was drawn off and distilled; 2 cc. of moist crotonaldehyde, boiling at 98°–106°, were obtained, but the main portion was a mixture of high-boiling as well as non-volatile red oils.

Similarly, 4 grams of aldol dissolved in 12 cc. of water containing 3 drops of 20 per cent sulphuric acid gave, after heating for 10 hours at 100°, in a sealed tube, no trace of aldehyde, 1.5 cc. of crotonaldehyde, 48 per cent of the theory, and a total of 1 gram of high-boiling and non-volatile reddish gum.

It is evident from the work of Nef that the function of the small amount of alkali or of sulphuric acid used in the experi-

ments described above is to form temporarily with the aldol a salt,

$$CH_3CH(OM)CH_2CHO,$$

or an ester,

$$CH_3CH(OSO_2OH)CH_2CHO,$$

which, being *relatively more dissociated* into the alkylidene derivative,

$$CH_3C< \quad \text{and} \quad HOM \quad \text{or} \quad H_2SO_4$$
$$O:CHCH_2$$

than the mother substance, enables the intramolecular transformation of the methylene derivative,

$$CH_3C<$$
$$O:CH—CH—H$$

into crotonaldehyde

$$CH_3CH:CHCHO,$$

to take place *more rapidly* because of increased concentration.

*On the Behavior of Acrolein and of Hydracrylic Aldehyde towards Alkalies.*

A thorough investigation of the action of traces of mild and caustic alkalies on acrolein and on hydracrylic aldehyde was extremely desirable[1] and I therefore took up this study under Dr. Nef's guidance. The statement of Nef that these compounds are split under the conditions just named into crotonaldehyde, etc., was found to be incorrect. I have observed that all alkalies, both mild and caustic, when added in traces to a cold aqueous solution of acrolein invariably transform the substance quantitatively, and with marked evolution of heat, into an insoluble, amorphous polymer, which is perfectly analogous to the one obtained by Nef with acrolein and barium hydroxide. These polymers are neutral to sodium carbonate, but dissolve easily in 10 per cent sodium hydroxide and, after digesting for a short time at 100° and adding the calculated

[1] Ann. Chem. (Liebig), 335, 220.

amount of hydrogen chloride, an amorphous, very high-melting substance is deposited whose weight is about one-half that of the polymer originally taken. The same end result is obtained with hydracrylic aldehyde and sodium hydroxide, although in this case no insoluble acrolein polymer is first deposited from the alkaline solutions on standing in the cold. These results made it impracticable to proceed further with the investigation and I therefore simply converted the remainder of my acrolein into hydracrylic aldehyde, in order to prove that this substance gives pentaerythrose, etc., when treated, in aqueous solution, with 2 mols. of formaldehyde, in the presence of traces of caustic alkali. All the acrolein used in my work was made from commercial glycerin and traces of phosphoric acid, according to Nef's directions.[1] I have found, after many trials, with 1 to 10 grams of phosphoric acid, that it is best to use 3 grams of phosphoric acid, sp. gr. 1.73, for every 100 grams of glycerin taken and to heat the mixture at first for 2.5 hours in a bath kept at 220°–240°, and then for one-half longer at 260°–300°. The yield of pure acrolein was regularly 10 grams for every 100 grams of glycerin taken, and the operation can be carried out successfully and without appreciable frothing by using 500 grams of glycerin at one time.

*On the Acrolein Polymers.*—Twenty-three and five-tenths grams of acrolein, b. p. 52°–58°, were dissolved in 184 cc. of water and 0.1 gram of potassium carbonate dissolved in 2 grams of water was then added in the cold. Turbidity sets in immediately and soon a large amount of a white substance separates out as a voluminous solid. The odor of acrolein was practically all gone after 18 hours' standing, but to insure complete transformation the mixture was treated with 0.1 gram more of potassium carbonate and allowed to stand 24 hours longer. Thus 22.5 grams of a white, amorphous substance, obviously, from its properties, polymeric acrolein were obtained. The polymer is insoluble in hot water, ligroin, ether, carbon bisulphide, benzene, glacial acetic acid; it dissolves easily in warm 95 per cent alcohol. On warming with dilute acids or alkalies, as well as on direct heating up

[1] Ann. Chem. (Liebig), 335, 221, foot-note.

to 100° and above, a strong odor of acrolein is at once noticed. My substance softened at 83° and decomposed, with gas evolution, at 94°–95°, whereas the perfectly analogous compound obtained by Nef[1] softens at 115° and decomposes at 128°–130°. It is quite possible that the polymers are space isomers, but as neither product could be obtained in the crystalline form the homogeneous nature of each is uncertain. Both dissolve, however, on warming in 10 per cent sodium hydroxide and give, apparently, the same end product.

In repeating the experiment with 18.2 grams of acrolein, dissolved in 56 grams of water, it was observed that by an addition of 1 gram of potassium carbonate, dissolved in 4 cc. of water, a sudden and marked rise of temperature took place and that the transformation into the polymeric acrolein was practically complete in 15 minutes; 15 grams of amorphous substance, softening at 81° and decomposing at 94°–95°, were thus obtained.

Thirteen and eight-tenths grams of the polymeric acrolein were now heated in a distilling flask and the temperature of the surrounding bath was finally raised to 190°–220°; much tar formation took place and the distillate, 4.2 grams, gave, on fractionation, 2 cc. of acrolein boiling at 52°–60°.

As already mentioned, these polymers, as well as acrolein and hydracrylic aldehyde, all give red solutions on warming with 10 per cent sodium hydroxide; no crotonaldehyde nor its condensation products can have been formed in these cases for the solutions remain clear and give no aldehyde resin on long boiling.

After heating for 12 hours at 100° and then neutralizing with the calculated amount of hydrogen chloride, a light brown, flocculent precipitate is obtained. The weight in all cases was found to be about one-half of that of the substance taken. This precipitate is likewise amorphous, insoluble in water and practically all organic solvents and does not melt when heated up to 180°. It is neutral to sodium carbonate but dissolves easily and without change in sodium hydroxide.

[1] *Loc. cit.*

*Pentaerythrose, $(CH_2OH)_2 : CCH:O$, from Mixtures of Formaldehyde and Acetaldehyde or Hydracrylic Aldehyde, Respectively.*

A solution containing 15 grams of aldehyde, 354 cc. of water and 87.6 grams of 35 per cent formaldehyde (3 mols.) was treated in the cold with 0.4 gram of powdered sodium hydroxide. No rise of temperature was noticed, but after 8 hours' standing the solution had become faintly acid; 0.4 gram more of sodium hydroxide was then added and, after standing over night, the same treatment was continued daily for 4 days, using, therefore, in all 3.2 grams of sodium hydroxide. The solution was now again faintly acid and the presence of formaldehyde could still be detected by a faint odor; the water was removed by distillation (25 mm.), heating, finally, on a boiling water-bath for 0.5 hour; 41.4 grams of thick, yellowish oil—crude pentaerythrose—remained in the distilling flask. A portion of the oil, 18.4 grams, was dissolved in 65.2 grams of acetic anhydride and then heated for 8.5 hours at 100°. The acylated gum, left after distilling off the acetic acid and anhydride (25 mm.), heating finally in a bath at 100°, was found to weigh 32.7 grams. It was freed from 4.53 grams of insoluble sodium salts by dissolving in 400 cc. of warm ether. The ethereal filtrate was then washed with 160 cc. of 10 per cent potassium carbonate and dried with calcium chloride. The ether was distilled off and the last traces present removed by heating at 100° (20 mm.); 27 grams of a yellowish, mobile oil remained, which is evidently acylated pentaerythrose, containing also some acylated pentaerythrite and acetylated $\beta,\beta'$-dihydroxyisobutyric aldehyde. The oil is insoluble or very sparingly soluble in water and all attempts to convert it into the solid state were fruitless. On distillation (30 mm.) 5.3 grams of the oil gave, with marked decomposition, 3.2 grams of distillate boiling at 215°–230°. Furthermore, the acylated oil, on treatment with phenylhydrazine, gave no well-defined derivative; the only thing left to do was to convert the oil back into pentaerythrose by hydrolysis with water. This was done by heating to 100° 3 times with 5

parts of water in periods of 10 hours each and distilling off the water and acetic acid after each operation under 20 mm., heating, finally, on a boiling water-bath. Twenty-nine and nine-tenths grams of acylated oil gave thus 17.8 grams, 16.1 grams and, finally, 15.5 grams of crude pentaerythrose as a highly viscous, yellowish oil. The oil is very soluble in cold water and alcohol, reduces Fehling's solution on warming, but all attempts to convert it into the solid state or into a crystalline derivative have, up to the present time, resulted in failure. That much pentaerythrose is present is proved, however, by the fact that the oil gives, on reduction with sodium amalgam in dilute acid solution,[1] a fair amount of pentaerythrite,[2] melting at 253°. For this purpose the crude pentaerythrose, obtained directly from the aqueous solution after condensation and subsequent removal of the water, was used; it contained, therefore, some sodium formate; 18.4 grams of gum were dissolved in 62.5 grams of water and treated, in the course of 6 hours, with 2.5 per cent sodium amalgam containing 9.3 grams of sodium, 1.5 times the theory, taking care to keep the solution at about 0° and faintly acid throughout the operation by continual addition of dilute sulphuric acid.

The water was then distilled off from the neutralized solution (20 mm.) and the salt residue, 67.5 grams, digested with 300 cc. of absolute alcohol, leaving 52.7 grams of insoluble salts. On cooling, the alcoholic filtrate gave 2.65 grams of pentaerythrite and on removing the alcohol entirely 9.6 grams of crystalline residue remained. The latter gave, on crystallization from a very small amount of water, 1.2 grams of a crystalline substance which melted at 170°–180°. The 12.25 grams of material soluble in the hot alcohol were finally resolved, by repeated fractional crystallization from water and alcohol, mainly into 2 products besides some unchanged pentaerythrose gum; namely, 3.2 grams melting at 220°–253°, from which 2.2 grams of practically pure pentaerythrite, m. p. 248°–253°, were obtained and 2.7 grams of substance melting between 170°–180°. It is extremely probable that this lower

[1] E. Fisher: Ber. d. chem. Ges., **23**, 3685.
[2] Tollens and Wigand: Ann. Chem. (Liebig), **265**, 322.

melting substance, which was also noticed by Tollens and Rave[1] in their work, is trihydroxytrimethylmethane,

$$(CH_2OH)_3 \vdots CH.$$

The analytical data given by Tollens and Rave, in fact, agree very well with those demanded by this compound. It must, therefore, be inferred that the crude pentaerythrose obtained in my experiments contains fairly large amounts of $\beta,\beta'$-dihydroxyisobutyric aldehyde.

The following experiment with hydracrylic aldehyde and 2 mols. of formaldehyde proves that in this case also large amounts of pentaerythrose[2] are formed:

Nineteen and six-tenths grams of hydracrylic aldehyde, made according to Nef's directions,[3] but not distilled and simply freed from water and acrolein by heating in a bath at 80° (20 mm.), were dissolved in 78.4 grams of water; 45.4 grams of 35 per cent formaldehyde and, thereupon, 14 cc. of 1 per cent sodium hydroxide were added in the cold. A rise of 5° in temperature was noticed during the following 30 minutes and after 24 hours the solution had become neutral to litmus; 0.14 gram more of sodium hydroxide was now added daily for 13 days, or a total of 1.96 grams in all.

The aqueous solution, which was practically neutral and had still a faint odor of formaldehyde, was now freed from water by distillation (20 mm.), heating finally in a bath at 100° for 0.5 hour; 35 grams of crude pentaerythrose gum, containing some sodium formate, were thus obtained. The gum was dissolved in 107 grams of acetic anhydride[4] and heated at 100° for 9 hours; after getting rid of the acetic acid and anhydride by distillation (25 mm.) on a boiling water-bath, 58.9 grams of acylated gum were obtained. This was freed from 5.66 grams of sodium salts by dissolving in 300 cc. of warm ether. On distilling off the ether and removing the last traces by heating for 2 hours in a bath at 100° (18 mm.), 49.35 grams of a mobile, reddish

[1] Ann. Chem. (Liebig), **276**, 59, foot-note.

[2] Cf. Klüger: Monats. Chem., **26**, 885.

[3] Ann. Chem. (Liebig), **335**, 219.

[4] Special experiments with hydracrylic aldehyde and acetic anhydride have proved that at 100° no acetyl derivative but a non-volatile, at 300° (20 mm.), condensation product is formed.

acylated oil, insoluble in water, were obtained—obviously acylated pentaerythrose containing small amounts of acetylated pentaerythrite and $\beta,\beta'$-dihydroxyisobutyl aldehyde.

*Hydrolysis of the Acylated Oil.*—The 49.35 grams of oil were now hydrolyzed by heating with 5 parts of water at 100°, for 10 hours, repeating the operation 3 times and removing the acetic acid, etc., formed by distillation (25–30 mm.) in a bath at 100°. The amount of non-volatile gum left after each treatment was 34 grams, 31.9 grams, and finally, 30.5 grams. The last portion obviously now consists mainly of pentaerythrose and shows a behavior which is in every way analogous to that shown by the crude pentaerythrose obtained from formaldehyde and acetaldehyde. It is a reddish, viscous gum, quite soluble in cold water and alcohol and reduces Fehling's solution on warming. Up to the present time all attempts to obtain a crystalline derivative, or to solidify the oil, have failed. The investigation of pentaerythrose will be continued in the near future. I wish especially to study also its oxidation products and to convert the crude pentaerythrose from hydracrylic aldehyde into pentaerythrite and trihydroxytrimethylmethane by means of sodium amalgam, in acid solution.

*On the Action of Aqueous Copper Acetate on the Hexoses.*

In view of the experimental difficulties presenting themselves in connection with the study of crude pentaerythrose and because of my desire to complete my studies during the present academic year, Dr. Nef suggested that I assist him in his study of the action of oxidizing agents on the sugars—a problem to which he has been devoting himself for over 2 years past.[1] The task assigned to me was the quantitative determination of the amount of cuprous oxide, carbon dioxide, formic, glycollic and oxalic acids formed from 100 grams of *d*-glucose, *d*-fructose and *d*-galactose by 8 hours' heating on a boiling water-bath with an excess, 10 mols., of aqueous copper acetate. Preliminary experiments by Nef, carried out in the autumn of 1904, had established the formation of the acids named except formic acid, and their relative amounts had, also

[1] Ann. Chem. (Liebig), **335**, 323-333.

in part, been ascertained by him. My own quantitative results confirm his observations in these particulars. The other acids formed in the oxidation with copper acetate, which give calcium salts very soluble in water and precipitated by alcohol and which constitute about 40 per cent of the total reaction products, are at present being investigated by Nef; it is obviously impossible to present a theory of the oxidation of hexoses until this work is completed.

*d-Glucose and Copper Acetate.*—Twenty grams of *d*-glucose, m. p. 140°–150°, dissolved in 50 grams of water, were added to a warm solution of 225 grams of crystallized copper acetate, $Cu(C_2H_3O_2)_2.H_2O$, 10 mols., in 2 liters of water. The mixture was heated for 8 hours on a boiling water-bath under a reversed condenser. This operation was repeated 5 times, and in all 99 grams of dextrose were taken. The amount of carbon dioxide given off with 10 grams of dextrose and a corresponding amount of aqueous copper acetate was determined in a special experiment, as follows: The mixture was heated for 8 hours on a boiling water-bath, during which period a steady stream of carbon dioxide-free air was passed through the solution and the gaseous products were drawn through 2 tall cylinders filled with saturated barium hydroxide solution; 5.46 grams of barium carbonate, well washed and dried at 100°, were obtained, which corresponds to 12.2 grams of carbon dioxide from 100 grams of dextrose. Nef obtained, in a similar experiment with 20 grams of dextrose, etc., after heating for 6 hours in an oil-bath at 100°–110°—at the higher temperature the reaction is more complete—13.2 grams of barium carbonate, corresponding to 14.75 grams of carbon dioxide from 100 grams of dextrose. It was noticed that most of the carbon dioxide, as well as the greater part of the cuprous oxide, is formed during the first hour's heating.

Nef obtained, in his experiment with 20 grams of dextrose, 64 grams of cuprous oxide, whereas the average amount obtained by me in 4 experiments was 59.6 grams for every 20 grams of *d*-glucose. It was proved by special experiments—by dissolving in hydrogen chloride, precipitating with hydrogen sulphide, etc.—that the cuprous oxide obtained was, in all

cases, practically free from cupric or cuprous oxalate. From these data the amount of oxygen taken up in the oxidation of *d*-glucose was 4.08 atoms in my experiments.

The aqueous filtrates from the cuprous oxide were now united, the copper still present in large amounts was precipitated by hydrogen sulphide and the filtrate freed from hydrogen sulphide by drawing air through the hot solutions under a reversed condenser. The water was then distilled off slowly under reduced pressure until the volume of the solution reached about 2 liters, whereupon small amounts of sulphuric acid, formed by the oxidation of the copper and hydrogen sulphides, were removed by digestion with small portions of barium hydroxide so that, finally, the solution contained traces of barium. The water in the aqueous filtrate was now removed by distillation (20 mm.) and to insure complete removal of the volatile fatty acids present the residual gum was again dissolved in water and the distillation, under reduced pressure, repeated, heating, finally, on a boiling water-bath for 0.5 hour.

As an end result, 99 grams of dextrose gave 63.5 grams of non-volatile gum and 17.185 liters of distillate, containing water, acetic and formic acids.

The amount of formic acid present in the distillate was determined quantitatively by H. C. Jones' method[1] with potassium permanganate—a method which depends upon the fact that acetic acid is not oxidized in sodium carbonate solution at 70°–80° with 0.1 N potassium permanganate, whereas, sodium formate, being relatively much dissociated according to

$$O : C\begin{matrix} H \\ \diagup \\ \diagdown \\ ONa \end{matrix} \rightleftharpoons O : C< + NaO—H,$$

is oxidized quantitatively to carbon dioxide under these conditions.

Preliminary experiments with much acetic acid and known quantities of formic acid proved that the method is perfectly

[1] THIS JOURNAL, 17, 539. Cf. Lieben: Monats. Chem., 14, 146. Peau de St. Gilles: Ann. de chim. et d. Phys., (3), 55, 388.

reliable; the results obtained, however, with the above-mentioned aqueous distillate are not absolutely final concerning the amount of formic acid present because the aqueous distillates, in the case of all hexoses used, were found to reduce Fehling's solution very slightly on vigorous boiling. This shows that some volatile sugar must be present, but I was unable to determine whether the product was formaldehyde or glycollic aldehyde; obviously, however, some of the permanganate must be used up in oxidizing this substance. Furthermore, it was ascertained by special experiment that the copper acetate used in all my work contained the following amount of reducible material: Copper acetate, 20 grams, were digested for 2 hours with 100 cc. of water, 100 cc. of saturated sodium carbonate solution and with 20 cc. of 10 per cent. sodium hydroxide and the solution was then filtered from the insoluble black copper oxide. The colorless filtrate was acidified and made up to 1 liter; 100 cc. of this solution were then made alkaline with sodium carbonate and treated with an excess of 0.1 N potassium permanganate at 70°–80°, for 0.5 hour; the solution was then acidified with sulphuric acid, treated with an excess of 0.1 N oxalic acid and titrated back with 0.1 N potassium permanganate. It was found thus that 12.52 cc. 0.1 N potassium permanganate are used up in oxidizing the impurities present in 20 grams of copper acetate; a corresponding correction, was, therefore, introduced, depending upon the amount of copper used in my oxidation experiments.

Thus the amount of formic acid present in the aqueous distillate, 17.185 liters, obtained from 99 grams of dextrose, was found to be 9.93 grams, as follows: One hundred cc. of the distillate were treated with sodium carbonate and an excess of 0.1 N potassium permanganate, at 70°–80°, for 0.5 hour; the solution was then acidified with dilute sulphuric acid, treated with an excess of 0.1 N oxalic acid and titrated back with 0.1 N potassium permanganate; 29.06 cc. of 0.1 N potassium permanganate were used up in this oxidation. Deducting the amount of permanganate necessary for the oxidation of the copper acetate used with 99 grams dextrose, we find that a total of 4317.6 cc. of 0.1 N potassium perman-

ganate is necessary for the oxidation of the formic acid. This corresponds, therefore, to 10.03 grams of formic acid for every 100 grams of dextrose taken.

*Determination of the Oxalic and Glycollic Acid in the Non-volatile Gum.*

The 63.5 grams of non-volatile acid gum obtained from dextrose was dissolved in hot water and digested for 2 hours with an excess, 64 grams, of powdered calcium carbonate. The 50.04 grams of insoluble calcium salts which were thus obtained were proved, by digestion with 100 cc. of water and 150 cc. of 30 per cent acetic acid, to consist of unchanged calcium carbonate and of 14.5 grams of calcium oxalate, corresponding to 8.9 grams of anhydrous oxalic acid.

0.2829 gram substance, dried at 100°–120°, gave, on ignition, 0.1081 gram CaO.

| | Calculated for $CaC_2O_4.H_2O$. | Found. |
|---|---|---|
| Ca | 27.45 | 27.29 |

The aqueous filtrate containing the soluble calcium salts and unchanged sugars was now concentrated, under reduced pressure, to a small volume and the calcium salts then precipitated by the addition of much alcohol. The salts which came down at first in a gummy state gradually get solid on rubbing with a pestle. The calcium salts still left in the aqueous alcoholic filtrate were then removed by further concentration and subsequent precipitation by alcohol. Thus a total of 46.8 grams of brown calcium salts was obtained. The quantity of calcium present, determined by ignition of a portion with sulphuric acid, was found to be 11.6 per cent. On dissolving the lime salts in a very small quantity of hot water a total of 5.57 grams of calcium glycollate, in 3 fractions, separated out on long standing. This corresponds to 3.25 grams of free glycollic acid and an analysis of the last 2 fractions, crystallized once more from water, gave the following result:

1.2161 grams substance, dried at 100°–120°, lost 0.3441 gram $H_2O$.

0.3086 gram of dry salt gave, on ignition, 0.0910 gram CaO.

| | Calculated for $Ca(C_2H_3O_3)_2.4H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 27.48 | 28.29 |
| CaO | 29.47 | 29.49 |

It is extremely probable that some calcium glycollate was still held in solution by the more soluble lime salts present, consequently my determinations of the amount of glycollic acid formed from the sugars are probably low both in the case of dextrose and of levulose.

On precipitating the lime in the aqueous filtrate from the 5.57 grams of calcium glycollate mentioned above, with the calculated amount of oxalic acid and then distilling off the water (20 mm.), heating, finally, in a bath up to 100°, 29 grams of gummy acids remained. These were converted, by digestion with 3 parts of acetic anhyhride at 100°, for 9 hours, etc., into 43.5 grams of acylated gum; only 26.2 grams of the gum dissolved on digestion with ether and the remainder, 17.3 grams of dark brown gum, gave, on threefold hydrolysis with 5 parts of water at 100°, 10.5 grams of dark brown acid tar.

The aqueous alcoholic filtrates obtained after the second precipitation of lime salts by alcohol were now concentrated to a small volume; it was proved by the addition of alcohol that only traces of lime salts are present. The amount of neutral, non-volatile gum present in the solution was, therefore, determined by distillation under reduced pressure, heating, finally, to 100°; 20.3 grams brown gum were thus obtained. It was shown, by titration with Fehling's solution, to contain 8.68 grams of dextrose, leaving, therefore, 11.62 grams of material undetermined. The presence of unchanged dextrose in the gum was established by the fact that a portion of the gum, when treated in the cold with aqueous phenylhydrazine acetate, gave a fair amount of the osazone of *d*-glucosone, m. p. 205°.

Finally, it should be mentioned that a special experiment with 9 grams of *d*-glucose and the corresponding amount of aqueous copper acetate was carried out in the usual manner, in which the absence of carbonic oxide, or of any other gaseous product except carbon dioxide, was established beyond a doubt.

*Levulose and Copper Acetate.*—One hundred grams of *d*-fructose, m. p. 102°–105°, were treated, in portions of 20 grams each, with aqueous copper acetate (10 mols.) for 8 hours in a boiling water-bath. The average amount of cuprous oxide obtained was 68.2 grams for every 20 grams of fruit sugar taken, whereas Nef obtained, in 1904, from a similar amount after 5.5 hours' heating in an oil- bath at 100°–110°, 71.5 grams of cuprous oxide. These results show that more oxygen is taken up in the burning of levulose than in that of dextrose. The difference must, however, be attributed in part to the fact that less unchanged sugar is found at the end of the experiment in the case of *d*-fructose, 2.9 per cent as compared with 8.8 per cent in the case of dextrose.

The amount of carbon dioxide formed was also found to be noticeably larger in this case, for 10 grams fruit sugar gave, on heating for 8 hours in a boiling water-bath with aqueous copper acetate, 7.25 grams of barium carbonate, which corresponds to 16.17 grams of carbon dioxide from 100 grams of levulose.

On removing the excess of copper in the combined filtrates from 100 grams of levulose by hydrogen sulphide, etc., 64.4 grams of non-volatile and very dark-colored gum remained in the distilling flask. This gave, on treatment with hot water, 10.25 grams of insoluble tar, and digestion of the aqueous filtrate with 80 grams powdered calcium carbonate, etc., gave 63.07 grams of insoluble calcium salts, which were proved to consist of unchanged calcium carbonate and of 10.65 grams of calcium oxalate, corresponding to 6.56 grams of anhydrous oxalic acid. The aqueous filtrate, containing the soluble calcium salts, gave, on concentration to about 100 cc. and after standing for 1 week, 7.68 grams of crude calcium glycollate; and this, on crystallization from 50 cc. of water, gave 3.4 grams of pure calcium glycollate in snow-white, bulky needles.

3.3817 grams substance, dried at 100°–120°, lost 0.917 gram $H_2O$.

0.2532 gram dried salt gave, on ignition, 0.0748 gram CaO.

| | Calculated for $Ca(C_2H_3O_2)_2.4H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 27.40 | 27.10 |
| CaO | 29.47 | 29.54 |

The aqueous filtrate from the 7.68 grams of crude calcium glycollate gave, on concentration and precipitation by alcohol, 48 grams of light-brown calcium salts which, on analysis, were found to contain 14.54 per cent of calcium; these gave, when digested with the calculated amount of oxalic acid, etc., 34.8 grams of non-volatile acid gums which were resolved by digestion with 500 cc. of ethyl acetate (6 times) and then with 5 parts of absolute alcohol (2 times) into 18.7 grams of gum soluble in ethyl acetate, 8.4 grams soluble in alcohol and 7.7 grams of dark-brown, tarry acid gum insoluble in these solvents.

In order to determine the amount of formic acid formed in the oxidation a duplicate experiment, carried out with 50 grams of levulose, gave the following result; the total aqueous distillate was found to require 3149.6 cc. of 0.1 N potassium permanganate for the oxidation of the formic acid, after making the usual corrections as stated above. From these data the amount of formic acid formed in the oxidation of 100 grams of levulose is found to be 14.50 grams. The non-volatile portion gave, on treatment with water, an excess of powdered calcium carbonate, etc., 4.89 grams of calcium oxalate, dried at 100°, corresponding to 3.01 grams of anhydrous oxalic acid.

0.3496 gram substance gave, on ignition, 0.1337 gram CaO.

| | Calculated for $CaC_2O_4.H_2O$. | Found. |
|---|---|---|
| Ca | 27.45 | 27.31 |

The aqueous filtrate containing the soluble calcium salts was concentrated to a small volume and the salts present precipitated by alcohol, in the usual manner. On digesting these with the calculated amount of oxalic acid, etc., 26.1 grams of brown, gummy acids were obtained. These gave, when digested successively with ethyl acetate and absolute alcohol, as above in the first levulose experiment, 12.5 grams of gum, soluble in ethyl acetate, 8.1 grams of gum soluble in alcohol and 5.5 grams of dark-brown insoluble acid tar.

On working up the aqueous alcoholic filtrates from the precipitated soluble calcium salts, by distillation under reduced pressure, heating, finally, in a bath at 100°, only 3.5 grams of

gum, practically free from calcium salts, were obtained; this was proved by titration with Fehling's solution, to contain 1.46 grams of unchanged levulose. Furthermore, an aqueous solution of the gum gave, on standing with aqueous phenylhydrazine acetate, the osazone of *d*-glucosone, m. p. 199°–202°. The experiment shows, therefore, that decidedly less unchanged sugar (2.9 per cent) remains in the case of levulose than in that of *d*-glucose (8.8 per cent) and *d*-galactose (8.5 per cent).

*Copper Acetate and d-Galactose.*—The amount of oxygen taken up and of carbon dioxide formed in the oxidation of *d*-galactose by aqueous copper acetate is noticeably less than in the case of fruit or grape sugar.

Fifty grams of *d*-galactose, m. p. 152°–154°, were treated in 3 portions with aqueous copper acetate, 8 hours, at 100°, in the usual manner. The average amount of cuprous oxide obtained fom 20 grams of *d*-galactose was only 55.3 grams and Nef obtained, in 2 experiments in 1904, an average of 58 grams on heating for 6 hours in an oil-bath at 100°–110°.

The amount of carbon dioxide obtained from 10 grams of *d*-galactose and the corresponding amount of aqueous copper acetate was only 0.463 gram (2.1 grams of barium carbonate) after 8 hours' heating on a boiling water-bath.

Titration of the aqueous distillate with potassium permanganate, in the usual manner, showed that a total of 2347.4 cc. of 0.1 N solution was necessary for the oxidation of the formic acid present. These data prove that 100 grams of *d*-galactose give 11 grams of formic acid. Forty-two and eight-tenths grams of non-volatile, gummy acids were obtained; these gave, on digestion with 40 grams of powdered calcium carbonate, etc., 36.2 grams of insoluble lime salts, containing, as shown by heating with dilute acetic acid, 9.38 grams of calcium oxalate, dried at 100°, and corresponding to 5.78 grams of anhydrous oxalic acid.

0.2321 gram substance gave, on ignition, 0.0892 gram CaO.

| | Calculated for $CaC_2O_4.H_2O$. | Found. |
|---|---|---|
| Ca | 27.45 | 27.45 |

In addition to this 0.72 gram of copper oxalate separated out from one galactose portion on standing, *i. e.*, before precipitating the copper in the filtrate from the cuprous oxide by hydrogen sulphide; therefore the amount of anhydrous oxalic acid obtained from 50 grams of *d*-galactose was 6.16 grams.

The aqueous filtrate from the insoluble calcium salts gave, on concentration and addition of alcohol, 29 grams of lime salts, dried at 80°–90°; these were found, by titration with Fehling's solution, to contain 1.19 grams of *d*-galactose, but the amount of calcium glycollate present was not determined in this case. Finally, the aqueous alcoholic filtrates from the precipitated lime salts were found, on distillation under reduced pressure, to contain 11.5 grams of gum; this material contained 3.06 grams of unchanged *d*-galactose, as determined by titration with Fehling's solution. Therefore, the total amount of unaffected galactose amounted to 4.25 grams or 8.5 per cent. The presence of this sugar was also established by treating a portion of the gum with aqueous phenylhydrazine acetate in the cold; on standing, a large amount of an osazone melting at 190° was obtained.

*The Action of Aqueous Copper Acetate on Formaldehyde, Formic, Glycollic and Oxalic Acids.*

The following experiments with aqueous copper acetate and the reagents named are of importance; first, they prove that the formic and carbonic acids obtained in the oxidation of the hexoses cannot possibly be attributed to the breaking down of a portion of the oxalic acid formed as an intermediate product; second, because they prove that the oxalic acid obtained cannot possibly come from an oxidation of glycollic acid; third, because they show, very decisively, that the carbon dioxide obtained from the hexoses cannot possibly come, to any appreciable extent, from an oxidation of formic acid:

(*a*) One hundred and twelve and five-tenths grams of copper acetate, dissolved in a liter of water containing 10 grams of formic acid (sp. gr. 1.22), were heated in a boiling water-bath for 6.5 hours under a reversed condenser. During the entire period a slow stream of air, free from carbon dioxide, was drawn steadily through the solution and then through 2 tall cylinders filled

with saturated barium hydroxide solution. A very small amount of carbon dioxide is slowly and steadily evolved, although no precipitation of cuprous oxide could be detected. Only 0.89 gram of barium carbonate, or 0.2 gram of carbon dioxide, was obtained.

(*b*) A similar experiment with 112.5 grams of copper acetate, 1 liter of water and 29 grams of 35 per cent formaldehyde gave, after heating in an air current for 6.5 hours on a boiling water-bath, no trace of barium carbonate, as shown by an absence of even turbidity in the cylinders containing the barium hydroxide.

(*c*) A mixture of 28 grams of copper acetate, 2 grams of glycollic acid, 2 grams of acetic acid and 1 liter of water was heated in a boiling water-bath for 6 hours in a manner entirely similar to (*a*) and (*b*), but no trace of cuprous oxide or carbon dioxide could be found.

(*d*) Two and five-tenths grams of crystallized oxalic acid, dissolved in water, were added to a warm solution of 28 grams of copper acetate, 25 grams of acetic acid and 900 grams of water. The oxalic acid is precipitated at once and completely as white cupric oxalate, and this is invariably the case, no matter what proportion of acetic acid is present. The mixture was now heated on a boiling water-bath for 8 hours under practically the same conditions as were employed in (*a*), (*b*) and (*c*); no change took place and no trace of carbon dioxide was evolved during this period.

This result is in marked contrast to that obtained with aqueous copper acetate and the 3 hexoses, where the oxalic acid found in the oxidation experiments remained entirely in the solution, *i. e.*, did not come down as cupric oxalate either with the cuprous oxide or subsequently from the filtrate which still contained much copper acetate even on long standing. It is, therefore, not improbable that the oxalic acid actually obtained from the hexoses, as stated above, may have been formed by the subsequent hydrolysis of an unknown intermediate product.

In conclusion, I wish to express a deep feeling of appreciation of the help and encouragement which Dr. Nef has given me in the whole course of this work.

# ACYL DERIVATIVES OF ORTHO- AND PARAMINOPHENOL.

By J. Bishop Tingle and L. F. Williams.

In the course of some other work which is now in progress in this laboratory we desired to carry out a series of experiments with ortho- and paraminophenol and with a considerable number of their mono- and diacyl derivatives. We have found that the recorded methods of preparing some of these compounds are not always consistent with each other and that in certain cases it was advisable to modify a published procedure in order to obtain a good yield; moreover, the properties of several of our products differ from those given in the literature; for these reasons, and also because we have synthesized a number of acyl derivatives which have not hitherto been described, we have decided to publish our results in the present paper, without waiting for the completion of the main part of our research.

The first step in our work was the conversion of ortho- and paranitrophenol into the corresponding monacetylaminophenols. Of the methods which have been suggested for this purpose that of Morse,[1] which consists in reducing the nitrophenols by means of acetic acid and tin, appeared to be the most convenient, but Zincke and Hebebrand[2] state that it failed to give them the desired compounds. Professor Morse informs us that he has received, in private communications, similar statements from other chemists, but that in the hands of some workers the method has given complete satisfaction. He suggested that these conflicting experiences might be accounted for by variation in the concentration of the acetic acid which was employed and that the best results would be obtained by the use of absolutely anhydrous acetic acid. Accordingly, we titrated some of the best glacial acetic acid obtainable and added to it recently distilled acetic anhydride, in quantity exactly sufficient to raise the acid content to 100 per cent. By means of this mixture and by carefully excluding moisture from the apparatus, we experienced no difficulty in obtaining a yield of

[1] Ber. d. chem. Ges., 11, 232.
[2] Ann. Chem. (Liebig), 226, 69.

each monacetylaminophenol equal to 50 per cent of the theoretical.

By adding concentrated hydrochloric acid in excess, to the crude solution of acetylorthoaminophenol, which is obtained after removal of the tin and evaporating the mixture to dryness, orthoaminophenol hydrochloride is readily formed.

From acetylorthoaminophenol, m. p. 201°, we prepared the following derivative, by the Schotten-Baumann method:

*Dibenzoylorthoaminophenol,* $C_6H_5COO^{1}C_6H_4^{2}NHCOC_6H_5$, crystallizes from alcohol in slender, white needles, melting at 180°. Its formation in this manner has not been previously recorded; it involves replacement of both acetyl and hydrogen by benzoyl groups.

The preparation of paranitrobenzoyl derivatives was effected by gradually mixing paranitrobenzoyl chloride, dissolved in benzene, with an aqueous solution of orthoaminophenol hydrochloride and adding, at intervals, small quantities of 20 per cent potassium hydroxide solution. The experiment was conducted in an atmosphere of carbon dioxide because free aminophenol is extremely sensitive to oxygen, especially in the presence of alkali. Operating under these conditions, we obtained 2 compounds, which were separated by means of acetone.

*Paranitrobenzoylorthoaminophenol,*

$HO^{1}C_6H_4^{2}NH^{1}COC_6H_4^{4}NO_2$, is deposited from alcohol in small, yellow crystals melting at 220°. It is tolerably readily soluble in acetone.

*Diparanitrobenzoylorthoaminophenol,*

$O_2N^{4}C_6H_4^{1}COO^{1}C_6H_4^{2}NH^{1}COC_6H_4^{4}NO_2$, is practically insoluble in the ordinary organic media. It crystallizes from nitrobenzene in slightly gray, feathery crystals, melting at 219°.

The corresponding metanitrobenzoyl derivatives were obtained in a similar manner to the para compounds.

*Metanitrobenzoylorthoaminophenol,*

$HO^{1}C_6H_4^{2}NH^{1}COC_6H_4^{3}NO_2$, is insoluble in benzene, but readily dissolves in hot acetone, from which it is deposited in small, yellow crystals, melting at 206°.

*Dimetanitrobenzoylorthoaminophenol,*
$O_2\overset{3}{N}C_6H_4\overset{1}{C}OO\overset{1}{C}_6H_4\overset{2}{N}H\overset{1}{C}O\overset{3}{C}_6H_4NO_2$, easily dissolves in benzene at the ordinary temperature and crystallizes from alcohol in light, flaky plates, which melt at 188°.

Under the same conditions as were employed in the case of paranitrobenzoyl chloride, except that the potassium hydroxide solution was only 10 per cent, phenylsulphonic chloride and orthoaminophenol hydrochloride yielded *phenylsulphoneorthoaminophenol,* $HO\overset{1}{C}_6H_4\overset{2}{N}HSO_2C_6H_5$. It was deposited from benzene or ether in small needles, which were almost white and melted at 141°. In another experiment carried out under similar conditions as nearly as they could be reproduced, except that we used a different preparation of phenylsulphonic chloride, we obtained only *diphenylsulphoneorthoaminophenol,* $C_6H_5SO_2O\overset{1}{C}_6H_4\overset{2}{N}HSO_2C_6H_5$, which was deposited from alcohol in slightly reddish columnar crystals melting at 134°. Georgesco states[1] that he obtained only diphenylsulphoneorthoaminophenol, m. p. 81°–83°, from phenylsulphonic chloride and orthoaminophenol, by the Schotten-Baumann reaction, but, in spite of several attempts, we were unable to prepare a compound with this melting point, or to detect its presence in our product. We regret that Georgesco's original paper is not accessible to us.

The formation of acetylparaminophenol from paranitrophenol was effected in the same manner as in the case of the ortho compound. Here, likewise, absolute acetic acid must be employed and moisture excluded from the apparatus. Under these conditions the preparation presents no special difficulties.

We also obtained the compound by the action of tin amalgam on the nitrophenol, in the presence of acetic acid of 100 per cent concentration. The experiments were carried out in an apparatus of special construction,[2] lent to us by Professor Morse. By means of an electric current the amalgam is produced continuously in the apparatus and various mechanical devices en-

[1] Chem. Centrabl., 1900, I., 543. Buletinul. Societatii de Scinte, 8, 668.
[2] *Vide* H. P. Straus: Dissertation, Johns Hopkins University, 1905.

sure constant contact between fresh amalgam and the nitro compound.

Acetylparaminophenol behaves towards concentrated hydrochloric acid like the ortho compound. It melts at 166°. The melting point, 179°, given by Morse,[1] is due to a printer's error. In the course of some experiments with this compound we heated it on the water-bath with alcohol, 95 per cent, and camphoroxalic acid. The product, after purification by means of ethyl acetate, strongly resembled the original acetaminophenol in its appearance, but melted at 170° instead of 166°. Closely agreeing analyses showed the content of carbon to be 0.5 per cent too high and that of nitrogen 0.9 per cent too low, *vide* p. 65. By heating at 105° the compound lost in weight to the extent of 0.43 per cent and then showed the same composition as at first and also, practically, the original melting point, 166°.5. Such behavior in this substance does not appear to have been observed before. We believe that it can be best explained as follows: A portion of the acetyl derivative is hydrolyzed by the water in the alcohol, under the catalytic influence of the camphoroxalic acid, and the mixture, or solid solution of acetyl derivative and aminophenol combines with some ethyl acetate. As this latter is not present in the crystals in any simple molecular ratio, it is probably to be regarded more as a solid solution than as ethyl acetate of crystallization. During the heating process acetylation once more takes place, by the action of free acetic acid present in the ethyl acetate and so, in this way and by the elimination of ethyl acetate, the original substance is regenerated.

By the action of acetyl chloride we obtained the diacetyl derivative, $CH_3COO\overset{1}{C_6}H_4\overset{4}{N}HCOCH_3$, m. p. 150°, which has been described by Ladenburg,[2] whose method of preparation was much less convenient.

Benzoyl chloride reacts with acetylparaminophenol under the conditions of the Schotten-Baumann method, yielding *N-Acetyl-O-benzoylparaminophenol*,

$$C_6H_5COO\overset{1}{C_6}H_4\overset{4}{N}HCOCH_3,$$

[1] Ber. d. chem. Ges., 11, 232.
[2] *Ibid.*, 9, 1529.

which is deposited from alcohol in white, feathery crystals melting at 166°.5. This difference in the action of benzoyl chloride on the ortho and paracetylaminophenols is interesting and suggestive (*vide* p. 52).

While this paper was in the hands of the printer, Reverdin[1] published a description of O-acetyl-N-benzoylparaminophenol and of O-benzoyl-N-acetylparaminophenol. Both compounds are stated to melt at 171°. Our melting points were determined with care and the purity of our compound is shown by analysis. Reverdin's experimental conditions differed somewhat from those employed by us and his analytical results comprise merely one nitrogen determination. We can only explain the difference in melting point by supposing that possibly his compound contained some monobenzoyl derivative. The coincidence in the melting point of his 2 substances is striking and suggestive.

Albert W. Smith, who prepared benzoylparaminophenol by the action of phosphorus pentachloride on *syn*-hydroxybenzophenoneoxime and also from benzoyl chloride and paraminophenol, gives the melting point as 205°–207°.[2] Our substance, also made from benzoyl chloride, melted at 227°.5.

When paranitrobenzoyl chloride is allowed to react with paraminophenol hydrochloride, under conditions similar to those described for the ortho compound (p. 52), two substances are formed: *Paranitrobenzoylparaminophenol*,

$$\overset{1}{HO}C_6H_4\overset{4}{N}H\overset{1}{C}O\overset{4}{C}_6H_4NO_2,$$

is deposited upon alcohol in small, glistening, orange-red, monoclinic crystals, melting at 258°. *Diparanitrobenzoylparaminophenol*,

$$O_2\overset{4}{N}C_6H_4\overset{1}{C}O\overset{1}{O}C_6H_4\overset{4}{N}H\overset{1}{C}O\overset{4}{C}_6H_4NO_2,$$

is obtained from solution in nitrobenzene in light yellow, microscopic crystals, melting at 264°.

Metanitrobenzoyl chloride also yields 2 compounds; *Metanitrobenzoylparaminophenol*, $\overset{1}{HO}C_6H_4\overset{4}{N}H\overset{1}{C}O\overset{3}{C}_6H_4NO_2$, which

[1] Ber. d. chem. Ges., 39, 3794 (1906).
[2] *Ibid.*, 24, 4042 (1891).

crystallizes from acetone in slender, light yellow needles, melting at 215°–216°. *Dimetanitrobenzoylparaminophenol*,

$$O_2\overset{3}{N}C_6H_4\overset{1}{C}OO\overset{1}{C}_6H_4\overset{4}{N}H\overset{1}{C}OC_6H_4\overset{3}{N}O_2,$$

is deposited from nitrobenzene as a light gray powder, melting at 264°–265°.

The action of phenylsulphonic chloride on paranitrophenol was studied under conditions similar to those employed with orthoaminophenol. Under these circumstances we obtained only *phenylsulphoneparaminophenol*, $HO\overset{1}{C}_6H_4\overset{4}{N}HSO_2C_6H_5$, which crystallizes from benzene in slender, slightly colored needles, melting at 156°.5 Georgesco[1] states that he obtained this compound and also diphenylsulphoneparaminophenol,

$$C_6H_5SO_2O\overset{1}{C}_6H_4\overset{4}{N}HSO_2C_6H_5,$$

and gives the melting point of the former as 125°–126° and of the latter as 150°–152°. We have repeated our experiments several times and, in the absence of details regarding the conditions which he used, we can only suggest, as the probable cause of the discrepancy between his results and ours, that he failed to purify his substances; this would explain why our *mono*-sulphone melts more than 4° higher than his *di*-sulphone. The analytical figures for our compound are given in the second part of the present paper. It may also be pointed out, in support of the correctness of our results, that they agree in every way with those reported by Troeger and Uhlmann[2] for the paratolylsulphones. They also obtained only monosulphones of ortho- and paraminophenol. Moreover, their ortho compound melts at 138°–139°, a little below the para derivative, which melts at 143°; the melting points of our compounds, 141° and 156°.5, respectively, correspond closely to these and show the same relationship. For convenience of comparison and by way of a summary, we show in the following table the simpler mono- and diacyl derivatives of ortho and paraminophenol. We have tried to make the list complete. The figures represent the melting points of the respective com-

[1] *Loc. cit.*

[2] J. prakt. Chem. [2], 51, 438, 441 (1895).

pounds. Those described for the first time in this paper are given in *italics*. It will be noticed that out of a total of 30 substances included in the table, 12 have been prepared for the first time by us; of the remaining 18 we have prepared 2 by a new, simpler method, have shown that the existence of 2 is decidedly doubtful and have corrected the melting point of another one:

*Table Showing the Simpler Acyl Derivatives of Ortho- and Paraminophenol.*

| | Orthoaminophenol. | | Paraminophenol. | |
|---|---|---|---|---|
| Name of acid radical. | Monacyl derivative. | Diacyl derivative. | Monacyl derivative. | Diacyl derivative. |
| Acetyl | 201° | 123°–124° | 166° | *150°*[1] |
| Acetyl-benzoyl | | | | *166°.5* |
| Acetyl-ethylsulphonyl | | | | 136° |
| Acetyl-picryl | | | | 165° |
| Acryl | 123°–124° | | | |
| Benzoyl | 167° | *180°*[1] | *227°.5*[2] | 233°–234° |
| Benzoyl-acetyl | | | | 171° |
| Chloracetyl | 136° | | | |
| Metanitrobenzoyl | *206°* | *188°* | *215°–216°* | *264°–265°* |
| Methylsulphonyl | | | 89°–90° | |
| Paranitrobenzoyl | *220°* | *219°* | *258°* | *264°* |
| Paratolylsulphonyl | 138°–139° | | 143° | |
| Phenylsulphonyl | *141°* | 81°–83°[3] | *156°.5* | 150°–152°[3] |
| Picryl | | *134°* | 174° | |

A number of experiments at 0°, at the ordinary temperature and at 240°–250° have been made in order to obtain tribenzoyl derivatives of ortho- and paraminophenols. In every case without success.

EXPERIMENTAL.

*Preparation of Orthoacetoaminophenol.*—Orthonitrophenol (12 grams, 1 mol.) was mixed in a capacious, round-bottomed flask with glacial acetic acid, 50 grams = 10.5 mol., to which sufficient recently distilled acetic anhydride had been added to bring the acid content to 100 per cent. The flask was attached to a long reversed condenser, suitably protected from the moisture

[1] Prepared by new method.
[2] Previous melting point corrected.
[3] Existence doubtful.

of the atmosphere and the contents of the flask were heated until the nitrophenol had dissolved. To this solution granulated tin, 15 grams, was added. The reduction commenced immediately and the action quickly became very vigorous. It is desirable to allow the reaction to proceed as rapidly as is possible without loss of substance. As soon as the action moderates, a second portion of tin, 15 grams, is added and, if necessary, external heat is applied to bring practically all of the metal into solution. The liquid is now poured into 2 liters of water, the mixture warmed and a current of hydrogen sulphide passed into it until no further precipitate of stannous sulphide takes place. Sometimes it is convenient to filter the liquid through cheese cloth before all the tin has been thrown down and then, later, to make a final filtration through paper.

The clear filtrate is concentrated until crystals appear; after being cooled the crystals are drained and recrystallized twice fom 95 per cent alcohol. The compound melts at 201°, as stated by Morse[1] and by Ladenburg.[1] This yield is 40–45 per cent of the theoretical.

*Preparation of Orthoaminophenol Hydrochloride.*—This compound is readily obtained by adding an equal volume of concentrated hydrochloric acid to the clear filtrate from the stannous sulphide and then evaporating to a small bulk. Should this concentrated liquid have the odor of acetic acid, more hydrochloric acid is added and the heating repeated until all acetic acid has been expelled. The hydrochloride readily forms crystals and may be purified by recrystallizing twice from water, with the addition of a little animal charcoal. It has no melting point within the range of our thermometers. The yield is about 50 per cent of the theoretical.

*Action of Benzoyl Chloride on Orthoacetaminophenol.*—The acetaminophenol, 14 grams = 1 mol., was dissolved in warm water and mixed with benzoyl chloride, 20 grams = 1⅜ mol. The liquids were well shaken and to them was added, in small portions, sufficient aqueous solution of potassium hydroxide, 10 per cent, to produce a permanent alkaline reaction. A precipitate which formed, finally, was removed, washed with

[1] *Loc. cit.*

water and recrystallized from alcohol. It is deposited in slender white needles, which melt at 180° and were found to consist of *dibenzoylorthoaminophenol.* The yield was excellent.

Analysis:

I. 0.1455 gram substance gave 0.4032 gram $CO_2$ and 0.0674 gram $H_2O$.

II. 0.1822 gram substance gave 7.7 cc. N at 22° and 760 mm.

| | Calculated for $C_6H_4\langle^{OCOC_6H_5(1)}_{NHCOC_6H_5(2)}$ | Found. I. | II. |
|---|---|---|---|
| C | 75.7 | 75.57 | . . |
| H | 4.73 | 5.14 | . . |
| N | 4.41 | . . | 4.65 |

*Action of Paranitrobenzoyl Chloride on Orthoaminophenol Hydrochloride.*—Free orthoaminophenol is readily colored by oxygen, consequently, experiments which involve the action of an alkali on the aminophenol hydrochloride were always carried out in an atmosphere of carbon dioxide. Paranitrobenzoyl chloride being a solid, it was found to be most convenient to employ it in benzene solution.

The aminophenol hydrochloride, 5 grams = 1 mol., was dissolved in water and mixed with a benzene solution of paranitrobenzoyl chloride, 12.7 grams = 2 mols. Potassium hydroxide, 20 per cent aqueous solution, was added gradually, the mixture being constantly shaken; this was continued until the liquid became permanently alkaline. The precipitate which formed was removed and, after being washed with water and dried, it was placed in a Soxhlet apparatus and extracted with acetone. The portion which dissolved was recrystallized from alcohol. It formed slightly yellow, light, feathery crystals, melting at 220°.

Analysis:

0.1677 gram substance gave 16.2 cc. N at 23°.5 and 764 mm.

| | Calculated for $C_6H_4\langle^{OH(1)}_{NHCOC_6H_4NO_2}$ $^{(2)\ (1)\ \ (4)}$ | Found. |
|---|---|---|
| N | 10.85 | 10.9 |

These results show that the body is *paranitrobenzoylorthoaminophenol.*

The compound that was insoluble in acetone was recrystallized from nitrobenzene; the deposited crystals, which were light and feathery, were washed with benzene. They melted at 219°. The substance, which proved to be *diparanitrobenzoylorthoaminophenol,* is practically insoluble in water, ethyl and methyl alcohols, ether, chloroform, ethyl acetate, benzene, toluene and ligroin.

Analysis:

I. 0.1495 gram substance gave 0.3214 gram $CO_2$ and 0.0443 gram $H_2O$.

II. 0.1409 gram substance gave 13 cc. N at 20° and 750 mm.

| | Calculated for $C_6H_3(OCOC_6H_4NO_2)(NHCOC_6H_4NO_2)$ | Found. I. | II. |
|---|---|---|---|
| C | 58.96 | 58.63 | . . |
| H | 3.19 | 3.29 | . . |
| N | 10.31 | . . | 10.4 |

The total yield of these 2 compounds was 80–90 per cent of the theoretical, in the ratio of 3 parts mono- : 5 parts of the dinitrobenzoyl derivative.

*Action of Metanitrobenzoyl Chloride on Orthoaminophenol Hydrochloride.*—The experiments with these compounds were carried out under exactly the same conditions as those with paranitrobenzoyl chloride which are described above. We worked with 10 grams (1 mol.) of the hydrochloride and 21.4 grams (1.7 mol.) of the acid chloride. The product of the reaction was extracted with benzene in a Soxhlet apparatus. The residue, insoluble in benzene, was dissolved in acetone, from which it separated in small, yellowish crystals, which melted at 206° and were found to consist of *metanitrobenzoylorthoaminophenol.*

Analysis:

I. 0.1541 gram substance gave 0.3434 gram $CO_2$ and 0.0600 gram $H_2O$.

II. 0.1108 gram substance gave 10.6 cc. N at 24° and 758 mm.

| | Calculated for $C_6H_4(OH(1))(NHCOC_6H_4NO_2(2\,1\,3))$ | Found. I. | II. |
|---|---|---|---|
| C | 60.46 | 60.77 | . . |
| H | 3.87 | 4.32 | . . |
| N | 10.85 | . . | 10.69 |

The second product of the reaction, which was soluble in benzene, was purified by solution in alcohol, from which it was deposited in light, feathery crystals with a slight pinkish tinge. It melted at 186° and proved to be *dimetanitrobenzoyl-orthoaminophenol.*

Analysis:

I. 0.1165 gram substance gave 0.2504 gram $CO_2$ and 0.0418 gram $H_2O$.

II. 0.1307 gram substance gave 12.2 cc. N at 23° and 759 mm.

| | Calculated for $C_6H_4(OCOC_6H_4NO_2(1\,2\,3))(NHCOC_6H_4NO_2(2\,1\,3))$ | Found. I. | II. |
|---|---|---|---|
| C | 58.96 | 58.61 | . . |
| H | 3.19 | 3.98 | . . |
| N | 10.31 | . . | 10.5 |

The total yield of these 2 compounds was about 80–90 per cent of the theoretical, of which rather more than half consisted of the dinitrobenzoyl derivative.

*Action of Phenylsulphonic Chloride on Orthoaminophenol Hydrochloride.*—These experiments were carried out under similar conditions to those employed in the case of paranitrobenzoyl chloride, *vide* p. 59. It was, of course, unnecessary to use benzene. We took 5 grams (1 mol.) of the hydrochloride and 12 grams (2 mols.) of the sulphonic chloride in each experiment; the concentration of the potassium hydroxide solution was 10 per cent. The crude, solid product of the reaction was dried and extracted with benzene in a Soxhlet apparatus, to remove a small quantity of tarry matter. After evaporation of the benzene the material which had dissolved in it was recrystallized from ether, being deposited in slender, pale-pink crystals, which are readily soluble in alcohol and melt at 141°.

It proved to be *phenylsulphoneorthoaminophenol.* The yield of purified product was about 70 per cent of the theoretical.

Analysis:

I. 0.1101 gram substance gave 0.2346 gram $CO_2$ and 0.0469 gram $H_2O$.

II. 0.1347 gram substance gave 6.8 cc. N at 24°.5 and 763 mm.

III. 0.2302 gram substance gave 0.2216 gram $BaSO_4$.

| | Calculated for $C_6H_4\langle^{OH(1)}_{NHSO_2C_6H_5(2)}$ | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 57.83 | 58.14 | . . | . . |
| H | 4.41 | 4.73 | . . | . . |
| N | 5.5 | . . | 5.51 | . . |
| S | 12.88 | . . | | 13.22 |

In another series of experiments in which we used 2.9 grams (1 mol.) of orthoaminophenol hydrochloride and 4 grams of phenylsulphonic chloride (1.25 mol.) with 10 per cent potassium hydroxide, the other conditions being as nearly as possible identical with those described above, we obtained only *diphenylsulphoneorthoaminophenol.* In other experiments in which the proportions of reacting substances were exactly the same as those used in the preparation of the monosulphone we again obtained merely the disubstituted compound. The only cause of this difference in behavior, which we have been able to detect, is in the phenylsulphonic chloride, two samples of which were at our disposal. Both of these were in Kahlbaum's original packages, but one always gave us the mono- and the other the disubstituted compound. This latter substance crystallizes from alcohol in reddish rods which melt at 134°.

Analysis:

I. 0.1476 gram substance gave 0.2939 gram $CO_2$ and 0.0582 gram $H_2O$.

II. 0.2029 gram substance gave 6.5 cc. N at 24° and 751 mm.

III. 0.2174 gram substance gave 0.2548 gram barium sulphate.

IV. 0.1532 gram substance gave 0.1786 gram barium sulphate.

| | Calculated for $C_6H_4\langle^{OSO_2C_6H_5\ (1)}_{NHSO_2C_6H_5\ (2)}$ | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| C | 55.49 | 55.23 | . . | . . | . . |
| H | 3.85 | 4.38 | . . | . . | . . |
| N | 3.59 | . . | 3.46 | . . | . . |
| S | 16.47 | . . | . . | 16.10 | 16.01 |

We are indebted to Mr. Nirdlinger, of this laboratory, for Analysis IV.

A number of experiments were also made with a third sample of phenylsulphonic chloride which was likewise one of Kahlbaum's preparations. It had been in stock for some time before we used it. With orthoaminophenol hydrochloride and this compound we obtained what appeared to be mixtures of the mono- and disulphones, melting at 126°.8. The monosulphone melts at 141° and the disubstituted compound at 134°. Mixtures of the two melt at 118° and a mixture of monosulphone and of the third preparation mentioned above (m. p. 126°.8) melts at 121°.

The discrepancy between our results and those of Georgesco has already been pointed out, *vide* p. 53. We made several attempts to prepare his diphenylsulphone derivative by varying the experimental conditions and the proportion of phenylsulphonic chloride, but without success. The low melting-point of Georgesco's disulphone, 81°–83°, and its red color, make us very doubtful as to the purity of his substance.

*Preparation of Paracetoaminophenol.*—This compound was prepared from paranitrophenol exactly in the same manner as the ortho derivative (p. 57). A few experiments were made for us by Dr. C. W. Gray to determine whether it was advantageous to prepare paracetoaminophenol by the electrolytic reduction of paranitrophenol in acetic acid solution. As will be apparent from what follows, the ordinary meaning of the term "electrolytic reduction" is hardly applicable to the conditions under which we worked; the active reducing agent was tin amalgam, which was continuously produced under the influence of the electric current. Paranitrophenol, 9 grams, and acetic acid of 100 per cent concentration, 35 grams, were placed in the cathode vessel. A rod of pure tin was inserted into the

anode compartment. The 2 vessels were connected by means of mercury and the whole apparatus was mounted on a wooden stand, to which could be imparted an automatic, steady rocking motion. This apparatus was designed by Professor Morse and is practically identical with that fully described and illustrated by H. P. Strauss,[1] who worked under his direction. By the use of a graphite-coated, electric furnace, constructed according to the description of Morse and Frazer,[2] the cathode compartment could be heated to any desired temperature.

The reduction of the nitrophenol proceeded without difficulty under these conditions, and the product of the reaction was worked up in the same manner as that obtained by the use of acetic acid and granulated tin. The yield was about 40 per cent of the theoretical.

This acetyl derivative was purified by solution in water, from which it is deposited in colorless, well-formed, monoclinic crystals. These melt at 166°, as given by Friedlander.[3] Because of the varying statements in the literature regarding the melting point of this compound, it was further identified by analysis.

I. 0.1891 gram substance gave 0.4403 gram $CO_2$ and 0.1019 gram $H_2O$.

II. 0.2104 gram substance gave 17.8 cc. N at 20° and 767 mm.

| | Calculated for $C_6H_4\langle^{OH\ (1)}_{NHCOCH_3\ (4)}$ | Found. I. | II. |
|---|---|---|---|
| C | 63.57 | 63.44 | . . |
| H | 5.96 | 5.98 | . . |
| N | 9.27 | . . | 9.6 |

The yield was about 47 per cent of the theoretical.

In the course of some experiments with this substance we had occasion to heat it on the water-bath with a solution of camphoroxalic acid in 95 per cent alcohol. A crystalline product was obtained which closely resembled paracetaminophenol, but melted at 170°.

[1] Dissertation, Johns Hopkins University, 1905.

[2] THIS JOURNAL, 32, 93 (1904).

[3] *Loc. cit.*

Analysis:

I. 0.1343 gram substance gave 0.3150 gram $CO_2$ and 0.0716 gram $H_2O$.

II. 0.1429 gram substance gave 0.3357 gram $CO_2$ and 0.0766 gram $H_2O$.

III. 0.2843 gram substance gave 21.5 cc. N at 22°.5 and 760 mm.

IV. 0.1765 gram substance gave 13.3 cc. N at 21°.5 and 755 mm.

| | Calculated for $C_6H_4\langle^{OH(1)}_{NHCOCH_3(4)}$. | Calculated for $C_6H_4\langle^{OH(1)}_{NH_2(4)}$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|---|
| C | 63.57 | 66.05 | 64.09 | 64.07 | . . | . . |
| H | 5.96 | 6.42 | 5.92 | 5.95 | . . | . . |
| N | 9.27 | 12.84 | . . | . . | 8.35 | 8.32 |

A portion of the compound was heated at 105° until its weight became constant. The loss in weight amounted to 0.43 per cent. After this heating the substance melted at 166°.5, instead of 170° and, when analyzed, proved to be paracetaminophenol.

Analysis:

I. 0.1346 gram substance gave 0.3138 gram $CO_2$ and 0.0742 gram $H_2O$.

II. 0.2101 gram substance gave 17.5 cc. N at 20° and 752 mm.

| | Calculated for $C_6H_4\langle^{OH(1)}_{NHCOCH_3(4)}$. | Found. I. | II. |
|---|---|---|---|
| C | 63.57 | 63.58 | . . |
| H | 5.96 | 6.12 | . . |
| N | 9.27 | . . | 9.24 |

As stated more fully in the theoretical portion of this paper, we believe that the changes described above are due to the hydrolysis of a portion of the acetaminophenol; this would raise the carbon content; the percentage of nitrogen would, however, be reduced on account of the ethyl acetate which was retained, whereas this would produce much less effect on the carbon and hydrogen values. During the heating to drive off this ethyl acetate, acetylation of the hydrolyzed product took place, so that,

finally, we obtained acetaminophenol regenerated in a state of purity.

*Preparation of Paraminophenol Hydrochloride.*—This salt is readily prepared by adding to the clear filtrate from the stannous sulphide precipitate an equal volume of concentrated hydrochloric acid and evaporating to dryness. Should acetic acid be present towards the completion of the evaporation, more hydrochloric acid must be added and the heating continued. The product is purified by recrystallizing once or twice from water in the presence of a little animal charcoal. The yield of purified substance is about 45–50 per cent of the theoretical.

*Action of Acetyl Chloride on Paracetaminophenol.* — When these compounds are mixed, in equimolecular proportions, and gently heated, they quickly react. The product was crystallized from water. It melted at 150° and corresponded, in general properties, with the substance prepared by Ladenburg[1] from paraminophenol and acetic anhydride. The yield was practically quantitative.

*Action of Benzoyl Chloride on Paracetaminophenol.* — The experiments with these compounds were carried out under similar conditions to those employed in the case of orthoaminophenol. We worked in aqueous solution and used 10 per cent potassium hydroxide. The chloride and the acetaminophenol were employed in equimolecular proportion. The product of the reaction separated as a solid; after being washed it was recrystallized from alcohol, from which it was deposited in white, feathery crystals, melting at 166°.5. It is sparingly soluble in hot water but practically insolubie in cold. The compound proved to be *N-acetyl-O-benzoylparaminophenol.* The yield was about 90 per cent of the theoretical.

Analysis:

I. 0.1699 gram substance gave 0.4392 gram $CO_2$ and 0.0787 gram $H_2O$.

II. 0.1017 gram substance gave 5 cc. N at 19°.5 and 752 mm.

[1] Ber. d. chem. Ges., 9, 1529 (1876).

| | Calculated for $C_6H_4\langle^{OCOC_6H_5\ (1)}_{NHCOCH_3\ (4)}$ | Found. I. | II. |
|---|---|---|---|
| C | 70.58 | 70.44 | . . |
| H | 5.09 | 5.14 | . . |
| N | 5.49 | . . | 5.58 |

*Action of Paranitrobenzoylchloride on Paraminophenol Hydrochloride.*—These substances were allowed to react under conditions similar to those employed in the case of orthoaminophenol. The quantities taken were 5 grams (1 mol.) of the hydrochloride and 16 grams (2.5 mol.) of the acid chloride. The solid product was washed with water, dried and extracted in a Soxhlet apparatus with acetone. The greater portion remained undissolved. The substance soluble in acetone did not dissolve at all readily in ethyl alcohol, but it was deposited from methyl alcohol in small, orange-red crystals, melting at 258°. It also dissolves in ethyl acetate. We obtained the same compound, as the only product of the reaction, by intimately mixing finely divided paraminophenol hydrochloride, 3 grams (1 mol.), with the acid chloride, 4.2 grams (1.1 mol.), and heating in an open vessel at 160°. The resulting material was triturated in a mortar with 10 per cent sodium carbonate solution and then recrystallized from alcohol. The compound proved to be *paranitrobenzoylparaminophenol.*

Analysis:

I. 0.1384 gram substance gave 0.3067 gram $CO_2$ and 0.0548 gram $H_2O$.

II. 0.1852 gram substance gave 18.1 cc. N at 23°.5 and 770 mm.

| | Calculated for $C_6H_3\langle^{OH\ (1)}_{NHCOC_6H_4NO_2\ (4)\ (1)\ (4)}$ | Found. I. | II. |
|---|---|---|---|
| C | 60.46 | 60.43 | . . |
| H | 3.87 | 4.39 | . . |
| N | 10.85 | . . | 10.85 |

That portion of the product of the Schotten-Baumann reaction which was insoluble in acetone was crystallized from nitrobenzene; it formed a light yellow powder, melting at 264°. It

did not dissolve in water, ethyl alcohol, ether, methyl alcohol, ethyl acetate, nor in hot or cold aqueous potassium hydroxide solution. The substance proved to be *diparanitrobenzoylparaminophenol.*

Analysis:

I. 0.1067 gram substance gave 0.2312 gram $CO_2$ and 0.0343 gram $H_2O$.

II. 0.2285 gram substance gave 21 cc. N at 21° and 751 mm.

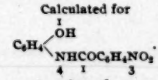
| | Calculated for | Found. I. | II. |
|---|---|---|---|
| C | 58.96 | 59.09 | . . |
| H | 3.19 | 3.57 | . . |
| N | 10.31 | . . | 10.12 |

The total yield of these compounds was about 80–90 per cent of the theoretical, in the proportion of approximately 3 parts of the mono- : 5 parts of the diacyl derivative.

*Action of Metanitrobenzoyl Chloride on Paraminophenol Hydrochloride.*—The hydrochloride, 5 grams (1 mol.), in aqueous solution, was mixed with the acid chloride, 12.8 grams (2 mols.), dissolved in benzene, and aqueous potassium hydroxide, 20 per cent solution, was added. The conditions of the experiment were exactly like those described for paranitrobenzoyl chloride and orthoaminophenol hydrochloride, *vide* p. 59. The solid product of the reaction, after being washed with water and dried, was extracted in a Soxhlet apparatus with ethyl acetate. The portion which dissolved in this solvent crystallized from acetone in slender, light yellow needles, melting at 215°–216°. It was sparingly soluble in alcohol and proved to be *metanitrobenzoylparaminophenol.*

Analysis:

0.1612 gram substance gave 0.3588 gram $CO_2$ and 0.0627 gram $H_2O$.

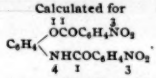
| | Calculated for  | Found. |
|---|---|---|
| C | 60.46 | 60.70 |
| H | 3.87 | 4.32 |

That portion of the reaction product which did not dissolve in ethyl acetate was purified by solution in nitrobenzene, from which it was deposited as a gray powder, melting at 264°–265°. It was insoluble in all the ordinary organic media and consisted of *dimetanitrobenzoylparaminophenol.*

Analysis:

I. 0.1764 gram substance gave 0.3824 gram $CO_2$ and 0.0599 gram $H_2O$.

II. 0.2342 gram substance gave 22.6 cc. N at 26° and 760 mm.



| | Calculated for | Found. | |
|---|---|---|---|
| | | I. | II |
| C | 58.96 | 59.12 | . . |
| H | 3.19 | 3.77 | . . |
| N | 10.31 | . . | 10.39 |

The total yield of these 2 compounds was 80–90 per cent of the theoretical, in the ratio of about 1 part mono-: 2 parts of dimetanitrobenzoyl derivative.

*Action of Phenylsulphonic Chloride on Paraminophenol Hydrochloride.*—The work with these substances was carried out exactly as in the case of the corresponding experiments with orthoaminophenol, *vide* p. 61. The quantities employed were 5 grams (1 mol.) of the hydrochloride and 12 grams (2 mols.) of the acid chloride. The solid product of the reaction was treated with benzene; a small portion of insoluble tarry matter remained. The part which dissolved was crystallized from ether and deposited in slender, white needles, melting at 156.5. It is readily soluble in alcohol, and consisted entirely of *phenylsulphoneparaminophenol* irrespective of which of the three samples of sulphonic chloride was employed, *vide* p. 62. An experiment was made with a different proportion of sulphonic chloride but the product was identical with the one first obtained.

Analysis:

I. 0.1201 gram substance gave 0.2555 gram $CO_2$ and 0.0542 gram $H_2O$.

II. 0.1624 gram substance gave 8.3 cc. N at 27° and 758 mm.

III. 0.2301 gram substance gave 0.2189 gram $BaSO_4$.

IV. 0.2202 gram substance gave 0.2086 gram $BaSO_4$.

| | Calculated for $C_6H_4\langle^{1\,OH}_{4\,NHSO_2C_6H_5}$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| C | 57.85 | 58.01 | . . | . . | . . |
| H | 4.41 | 5.01 | . . | . . | . . |
| N | 5.5 | . . | 5.45 | . . | |
| S | 12.88 | . . | . . | 12.01 | 13.01 |

Analysis IV was made for us by Mr. Nirdlinger, of this laboratory.

The yield was 70–80 per cent of the theoretical.

All our efforts to prepare a diphenylsulphone were unsuccessful.

Mr. Marshall P. Cram has been good enough to carry out for us a number of experiments with the object of obtaining *triacyl derivatives* of ortho and paraminophenol. As they have, unfortunately, not been attended with success they will be described very briefly. Orthoaminophenol hydrochloride, 7.25 grams (1 mol.), and benzoyl chloride, 50 grams (7 mol.), were mixed and treated with potassium hydroxide, 23 grams (8 mol.), in 15 per cent aqueous solution. The mixture was allowed to remain at the ordinary temperature for 3 weeks. In a second experiment, similar to the above, the materials were allowed to remain for 3 weeks, at 0°. Two further experiments were made at the ordinary temperature and at 0°, respectively, using pyridine, 100 cc., instead of the potassium hydroxide. Finally, all 4 experiments were repeated with paraminophenol hydrochloride instead of the ortho compound. The products from the experiments with potassium hydroxide were poured into water, filtered, and recrystallized from benzene. Only the dibenzoylaminophenols were obtained. From the aqueous filtrate benzoic acid alone could be isolated. The product from the pyridine experiments was extracted with ether, washed with water and the residue crystallized from benzene; it proved to be the dibenzoyl compound. The ethereal solution was extracted with dilute sulphuric acid and then evaporated; the residue was a mixture of benzoic and monobenzoylaminophenol.

Experiments were next tried at a high temperature. Dibenzoylparaminophenol, 72 grams, was mixed with dehydrated

sodium benzoate, 2.7 grams, 1 drop of concentrated sulphuric acid and a large excess of benzoyl chloride, 11.4 grams, and heated in a sealed tube for 1.5 working days, at 240°. A portion which was removed and tested showed that no reaction had taken place, consequently the heating was continued for another day, at 250°. This treatment caused incipient decomposition. Only the unchanged disubstitution derivative could be obtained from the product. A similar experiment was made with dibenzoylorthoaminophenol, but the conditions of heating were 1.5 days, at 240°. The result was similar to that obtained with the para compound.

JOHNS HOPKINS UNIVERSITY,
June, 1906.

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## ON THE SALTS OF TAUTOMERIC COMPOUNDS.

[EIGHTH COMMUNICATION ON URAZOLES.]

*Preliminary Paper.*

BY S. F. ACREE.

For several years the writer has been investigating[1] the reactions of some tautomeric substances and their salts, especially in the urazole series,[2] with the hope of securing more light on the behavior of these interesting and peculiar substances. The work on the reactions of the salts of some tautomeric substances has reached the point where a preliminary notice is desirable. The investigations will be continued in this laboratory and a more detailed account of the results will be published later. This paper deals only with the metallic salts of tautomeric compounds which are acids, and work on the acid salts of tautomeric substances which are bases will be published later.

The urazoles contain amide groups and exist in solutions in the following states of equilibrium: $C$, $C^{I}$, etc. represent the concentrations and $K$, $K^{I}$, etc., the equilibrium constants.

$$(1)\quad \underset{C}{\overset{+}{H}} + \underset{C^{I}}{\overset{-}{N}}(R)COR \underset{K}{\rightleftharpoons} HN(R)COR \underset{K^{II}}{\rightleftharpoons}$$

[1] The writer is indebted to the Carnegie Institution of Washington for aid in this work.

[2] THIS JOURNAL, 27, 118; 31, 185; 32, 606. Ber. d. chem. Ges., 38, 553; 36, 3139; 37, 184, 618.

$$\underset{C^{III}}{RN : C(OH)R} \rightleftharpoons \underset{K^{I}}{RN : C(R)\overset{-}{O} + \overset{+}{H}} \qquad \underset{C^{IV}}{\phantom{RN : C(R)\overset{-}{O}}} \quad \underset{C}{\phantom{+ \overset{+}{H}}}$$

Mr. G. H. Shadinger has proved that the values of $C$, $C^{I}$, etc. $K$, $K^{I}$, $K^{II}$, etc., vary greatly with the individual urazoles and with the conditions of solution. When such a system is treated with a sodium hydroxide solution the following states of equilibrium[1] are formed according to the laws governing (1) and (2).

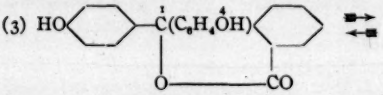
$$(2)\quad \underset{C_1}{\overset{+}{Na}} + \underset{C_1^{I}}{\overset{-}{N}(R)COR} \rightleftharpoons \underset{K_1}{\phantom{+}} \underset{C_1^{II}}{NaN(R)COR} \rightleftharpoons \underset{K_1^{II}}{\phantom{+}}$$

$$\underset{C_1^{III}}{RN : C(R)ONa} \rightleftharpoons \underset{K_1^{I}}{RN : C(R)\overset{-}{O} + \overset{+}{Na}} \qquad \underset{C_1^{IV}}{\phantom{RN : C(R)\overset{-}{O}}} \quad \underset{C_1}{\phantom{+ \overset{+}{Na}}}$$

It has been proved experimentally that equilibrium exists between $C^{II}$ and $C^{III}$ in (1) and between $C_1^{II}$ and $C_1^{III}$ in (2), and that $K^{II} = \dfrac{C^{II}}{C^{III}}$ and $K_1^{II} = \dfrac{C_1^{II}}{C_1^{III}}$. It therefore follows that $K_1$, $K_1^{I}$, and $K_1^{II}$ may vary greatly with different salts prepared from (1) and (2), a conclusion entirely justified by experiment. It further follows that even when $K$ or $K^{I}$ in (1) is very small, or zero, $K_1$ or $K_1^{I}$ in (2) may be comparatively large.

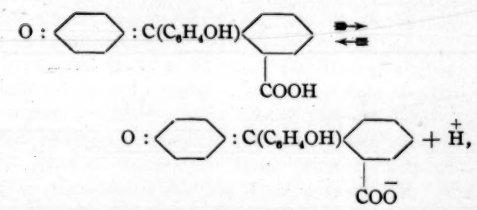
These relations probably hold for other tautomeric substances, such as ethyl acetoacetate types, nitrophenols, nitrosophenoles, phenolphthalein types, etc. In some cases, however, it may be found that the equilibrium is wholly between the ions.

Julius Stieglitz[2] and others believe that in substances of the phenolphthalein type the equilibrium may be expressed by the equations:

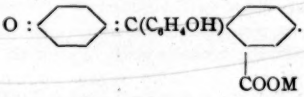
(3) 

[1] Baly, Marsden and Stewart: J. Chem. Soc., **89**, 966. Hantzsch and Ley: Ber. d. chem. Ges., **39**, 3149.

[2] J. Am. Chem. Soc., **23**, 1119.

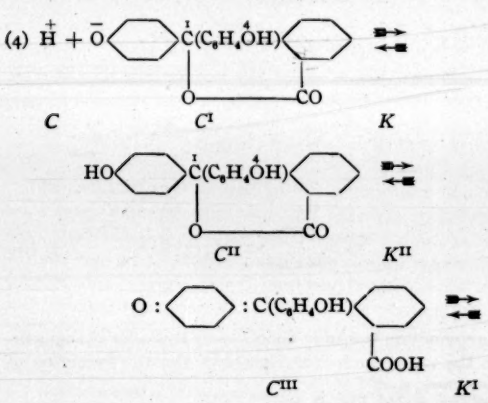


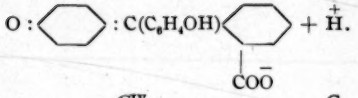
and that the simple salts have the constitution



They see in such an assumption the explanations of the color changes in indicators of this type.

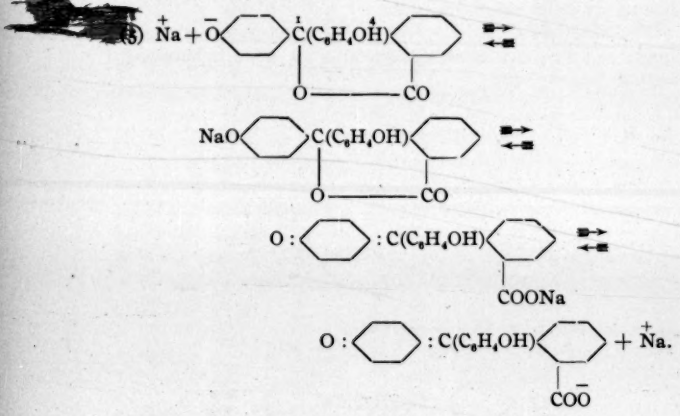
The writer feels, however, that such an explanation is inadequate and that the following equations are more in harmony with the known facts:





$C^{IV}$ $C$

Furthermore, the other phenol group is probably ionized to a very small extent. Since the affinity constant for benzoic acid,[1] for example, is K = 0.00006 and that of phenol[2] is K = 0.0000005, and further, since $C^{II}$ is undoubtedly much larger than $C^{III}$ (phenolphthalein is not colored in solution) it follows that the value of $C^{I}$ and the hydrogen ions corresponding must be considerable in comparison with $C^{IV}$. The reasoning employed above with the urazoles leads at once to the conclusion that the following set of equations express the equilibrium conditions present in solutions of the salts prepared by treating (4) with sodium hydroxide.

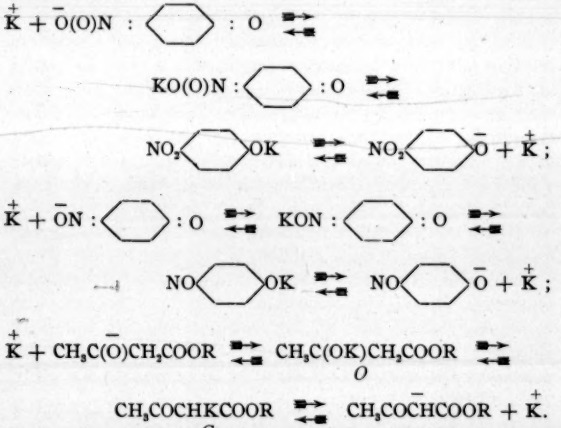


Such an explanation not only makes clear the color changes involved in the use of such indicators, but also the formation of

[1] Z. physik. Chem., 3, 418.
[2] Hantzsch; Ber. d. chem. Ges., 32, 3066.

the various phenol and carboxyl derivatives when the salts[1] of fluorescein, for example, are treated with alkyl halides.

Work in this laboratory on the alkylation of the salts of nitro and nitrosophenols, and of ethyl acetoacetate types, leads the writer to believe, contrary to the views of Nef,[2] Michael,[3] and Claisen[4] that the salts of these substances exist in solution in a condition that may be fairly represented in the following equations:[5]



This conception in regard to the constitution of acetoacetic ester salts, malonic ester salts and others of this type, make clear the formation of oxygen and carbon derivatives[6] when the various salts are treated with acid chlorides, alkyl halides, benzaldehyde, etc. Oxygen salts, *O*, have long been known to react with such acid chlorides and alkyl halides; the violence and rapidity

[1] Nietzki and Schröter: Ber. d. chem. Ges., **28**, 44; **30**, 175.
[2] Ann. Chem. (Liebig), **266**, 52; **276**, 200; **277**, 59, 83, etc.
[3] J. prakt. Chem., **37**, 469; **45**, 580; **46**, 189, etc.
[4] *Vide* Claisen's discussion, Ber. d. chem. Ges., **38**, 709.
[5] Kauffmann: Ber. d. chem. Ges., **39**, 1959. Hantzsch: *Ibid.*, **39**, 1084, 3072.
[6] Nef, Michael and Claisen: *Loc. cit.*

with which sodium phenyl,[1] a sodium-carbon compound, reacts with acid chlorides and alkyl halides, leaves no doubt that an acetoacetic ester salt with the constitution *C* would be very reactive. Furthermore, the writer has proved that the sodium pinaconates dissociate in ether and benzene solution as follows:

$$\underset{1}{(C_6H_5)_2C(ONa)C(ONa)(C_6H_5)_2} \underset{K}{\rightleftharpoons} \underset{2}{(C_6H_5)_2CO} + \underset{3}{(C_6H_5)_2CNa(ONa)}.$$

Reagents which will exert a *selective action* on one of the two forms of salts will aid greatly in determining if there are 2 salts in equilibrium. Benzaldehyde, carbon dioxide, etc., react readily with *3*, as they do with sodium phenyl, and *1* is transformed into *2* and *3* as fast as *3* is removed and *K* disturbed. On the other hand, acids, water, etc., react with both *1* and *3* and give a mixture of benzpinacone, about 90 per cent, benzophenone and benzhydrol. These reactions show equilibrium between the molecular forms, ions probably not coming into consideration in these reactions in benzene.

Another use of selective reagents in proving the presence of 2 tautomeric salts is the following: Phenylnitromethane and formylphenylacetic ester are tautomeric compounds, and both tautomeric forms have been isolated. If, now, the salts of these substances also exist in tautomeric forms in solution according to the following equation:

$$\overset{+}{Na} + \overset{-}{C_6H_5}CHNO_2 \rightleftharpoons \underset{A}{C_6H_5CHNaNO_2} \rightleftharpoons$$

$$\underset{B}{C_6H_5CH : N(O)ONa} \rightleftharpoons C_6H_5CH : N(O)\overset{-}{O} + \overset{+}{Na},$$

we should be able to select an acid weak enough to precipitate the more weakly acid tautomeric form, corresponding to the salt *A*, from solution, but not the stronger acid form corresponding to *B*; a strong mineral acid, however, would precipitate both tautomers. The experiments of Hantzsch and of Wislicenus amply verify this point. Carbonic acid precipitates the true

[1] Acree: THIS JOURNAL, 29, 588. Ber. d. chem. Ges., 37, 2753.

phenylnitromethane[1] and parabromphenylnitromethane from solutions of their alkali salts, whereas strong acids precipitate the more strongly acid isonitro forms, nearly pure. Likewise, carbonic acid precipitates the weakly acid *α*-formylphenylacetic ester[2] from solutions of its salts, whereas sulphuric acid precipitates the strongly acid *β*-form, mixed with a small amount of the *α*-form. These experiments show that both tautomeric salts are present in equilibrium, with the salt of the stronger acid form, *B*, in excess, as we should expect.

The experimental facts worked out by the writer, as well as all those of Claisen and Wislicenus, lead the writer to believe that all the syntheses analogous to the acetoacetic ester synthesis depend upon the reactions of tautomeric salts. To illustrate very briefly: It is believed that in the formation of acetoacetic ester from acetic ester and sodium ethylate the acetic ester first reacts with the sodium ethylate and forms a sodium salt of acetic ester which exists in 2 tautomeric forms. The sodium salt (2) then reacts vigorously with the acetic ester present, just as sodium phenyl or alkylmagnesium bromides do, and acetoacetic ester is formed:

$$CH_3COOC_2H_5 + NaOC_2H_5 \rightleftharpoons \begin{cases} (1)\ CH_2 : C(ONa)OC_2H_5 \\ \qquad\qquad \uparrow\downarrow \\ (2)\ CH_2NaCOOC_2H_5 \end{cases} + C_2H_5OH;$$

$$CH_3COOC_2H_5 + NaCH_2COOC_2H_5 \rightarrow CH_3C(ONa)(OC_2H_5)CH_2COOC_2H_5 \rightarrow CH_3C(ONa) : CHCOOC_2H_5 + HOC_2H_5$$

This conception is readily applied to other similar syntheses. The reactions of

$$BrMgCH_2COOC_2H_5 \quad \text{and} \quad CH_3CH(MgBr)COOC_2H_5,^3$$

which probably exist in the equilibrium illustrated by the above sodium salt, bear out the above conclusions completely. This subject will be treated in great detail in a subsequent article.

[1] Hantzsch and Schultz: Ber. d. chem. Ges., **29**, 699, 2251.
[2] Wislicenus: Ann. Chem. (Liebig), **291**, 147; **312**, 34.
[3] Meyer and Tögel: Ann. Chem. (Liebig), **347**, 55.

It is well known that when the silver salts of some amides are treated with alkyl halides at ordinary temperatures, oxygen esters are formed in large amounts, whereas the potassium salts yield, at higher temperatures, largely nitrogen esters. In some cases it has been proved that both are formed simultaneously. The copper salt of acetoacetic[1] ester, when treated with benzoyl chloride or acetyl chloride, yields a mixture of oxygen and carbon derivatives. If acetoacetic ester is heated with a mixture of silver oxide and an alkyl halide,[2] both oxygen and carbon derivatives are formed. In general, 2 different products have been found in such cases when the reaction products have been closely examined.

To account for such reactions several theories have been proposed:

I. The potassium and silver salts have different but definite structures. The potassium salt is a nitrogen compound and the silver salt is an oxygen compound (Comstock's older theory).[3]

II. When one salt yields with a certain reagent 2 products, one is formed directly and the second by rearrangement of the first (Wheeler's theory).[4] Wheeler assumed that all salts of the amides are oxygen derivatives, that these first yield O-esters which then form addition products with the alkyl halide and rearrange into N-derivatives.

III. When one salt yields with a certain reagent 2 products, one is formed by direct substitution of the metal and the other by formation of an unstable intermediate addition product (theories of Nef and of Michael).[5]

IV. The writer presents the following theory: A salt of a tautomeric compound reacts with an alkyl halide, or other reagent, and forms 2 compounds, because the tautomeric salt is really a mixture of 2 tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions. This reaction may, in certain cases, be complicated by the simul-

[1] Nef: Ann. Chem. (Liebig), **287**, 270.

[2] Lauder: J. Chem. Soc., **77**, 738. *Vide* also Nef: Ann. Chem. (Liebig), **276**, 200.

[3] Comstock and students: Ber. d. chem. Ges., **23**, 2274. THIS JOURNAL, **12**, 493; **13**, 514, 525.

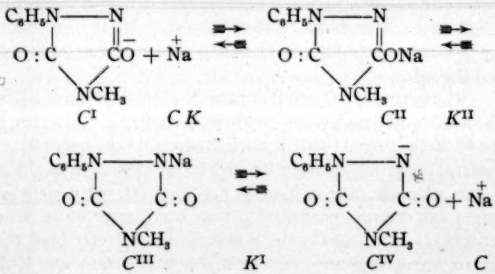
[4] Wheeler and students: *Ibid.*, **21**, 187; **23**, 135; **30**, 28.

[5] Nef and Michael: *Loc. cit.*

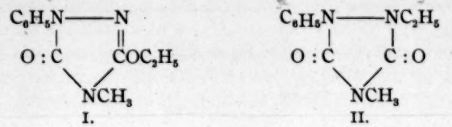
taneous rearrangement of one of the reaction products into the other or into some other product.

In order to test experimentally each of the above theories the writer and his co-workers, Dr. R. F. Brunel, Mr. G. H. Shadinger and Mr. J. M. Johnson, have studied quantitatively the alkylation of some salts of tautomeric compounds, such as 1-phenyl-4-methylurazole. We have a great deal of experimental evidence supporting the view that the salts of 1-phenyl-4-methylurazole exist in solution in the following equilibrium:

(VI.)



The values of $C$, $C^{I}$, ...., $K$, $K^{I}$, etc., vary with the salts, solvents, and the experimental conditions. When a salt of 1-phenyl-4-methylurazole is heated with ethyl iodide in water-alcohol, benzene, or ether solution, a mixture of 1-phenyl-4-methyl-3-ethoxyurazole, (I.), and 1-phenyl-4-methyl-2-ethylurazole, (II.), is formed:

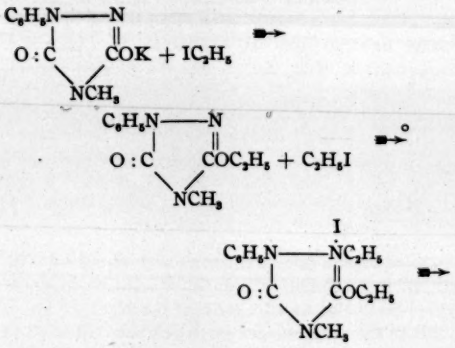


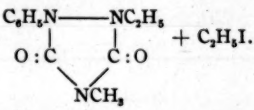
(A) The ratio of these 2 products varies with the salt. The potassium salt, in 40 per cent alcoholic-water solution, gives 90 per cent N-ethyl derivative and 10 per cent O-ethyl derivative. The barium salt in the same solvent gives 93.5 per cent N-ethyl

compound and 6.5 per cent O-ethyl compound. The silver salt in the same solvent gives 58.7 per cent O-ethyl derivative and 41.3 per cent N-ethyl derivative. The silver salt in ether gives 35 per cent N-ethyl compound and 65 per cent O-ethyl derivative. The measurement of these ratios at 22°, 60° and 90° shows that each ratio is nearly constant, or that the 2 side reactions have nearly the same temperature coefficient. The ratio, furthermore, does not change at different time intervals.

These facts render Comstock's older theory, I., that the silver salts are oxygen derivatives and the alkali salts nitrogen derivatives improbable. They further make it improbable that each salt is a mixture of 2 isomeric salts in a constant ratio for all the salts.

(B) Neither the O-ethyl nor the N-ethyl derivative rearranges into the other under any conditions studied. These conditions have been varied widely to include all the possible experimental conditions used in the alkylation experiments. Furthermore, since the ratio of N-ethyl and O-ethyl derivatives from a given salt does not change with time and temperature, Wheeler's theory (II.) that the O-ester is first formed directly from the salt, an oxygen compound, and then rearranges into the N-derivative, as represented by the following equations, cannot be used as a general explanation of such reactions:

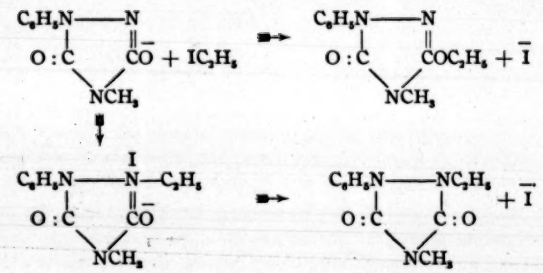




If we represent the concentrations of urazole salt, O-ester and N-ester, by *a*, *b* and *c*, respectively, the above equation takes the form $a \overset{1}{\rightarrowtail} b \overset{2}{\rightarrowtail} c$. As will be shown in detail later, if the reactions proceed according to this equation the products *b* and *c* cannot be formed in constant ratio. The only possible way for *b* and *c* to be formed in constant ratio is: first, for reaction 2 to be instantaneous, when the value of *b* would be zero; or, second, for reaction 2 to be instantaneously reversible, when *b* and *c* would exist in constant ratio. Neither the first nor the second assumption agrees with the experimental facts. Wheeler's theory is, therefore, improbable.

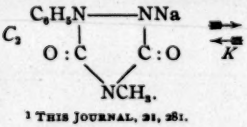
The writer believes that in the case of these urazoles the O-ester and N-ester are both formed independently from the 2 salts in (VI.). In some cases, however, as Wheeler showed, this reaction is undoubtedly complicated by the simultaneous rearrangement of one product, the O-ester, into another, the N-ester, and such cases will be made subjects of investigation in this laboratory. Wheeler did not, however, prove that the rearrangement of the O-ester was rapid enough to account for all of the N-ester formed in his experiments.

(C) The experimental evidence leads to the conclusion that only the urazole ion reacts with the ethyl iodide and that according to a reaction of the second order. According to Nef's and Michael's addition theories (III.) the salt has one structure and the O-ester and the N-ester should be formed according to the following reactions. The ethyl iodide may add to the double bond between the N and C, or add as illustrated:

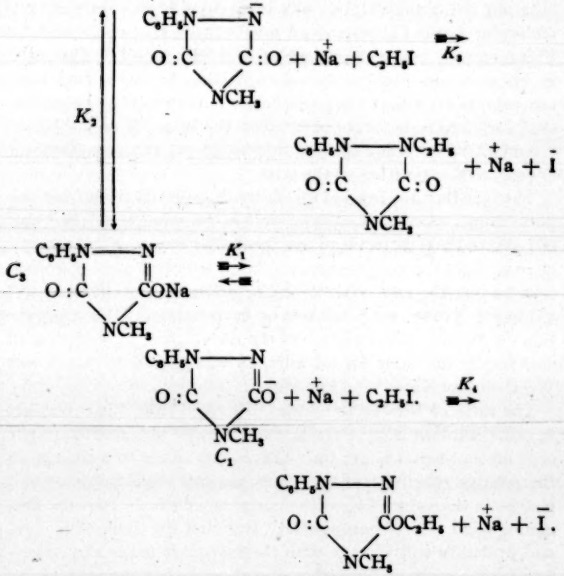


This theory, however, demands that under the same conditions of solution all the different salts should give a mixture of esters in which the ratio of the O-ester to the N-ester is a constant. The metallic ion should affect the course of the reaction no more than Remsen and Reid[1] found to be the case in the hydrolysis of amides by alkalies, or than has been found in many other cases. Different salts, however, as pointed out above, give widely different ratios of O-ester to N-ester, and hence Nef's and Michael's addition theories are inadequate. Another objection which might be brought up is the constancy of the ratio of O-ester to N-ester formed over a wide range of temperature. The potassium salt gives practically the same ratio at 22°, 60° and 90°. Two such different reactions demanded by the theories of Nef and Michael might be expected to have different temperature coefficients.

(D) The writer believes that the following equations represent fairly well the reaction of such tautomeric salts with alkyl halides, the changes or manner of reaction of the ethyl iodide not being considered here. This will be taken up later in detail.



[1] This Journal, 31, 281.



This theory of 2 salts in equilibrium predicts that various salts will give different values for $K$, $K_1$, $K_2$, etc., and different ratios of O-ester to N-ester, as has been actually found by experiment. It can be shown that the ratio $C : C_1$ increases with increase in the electronegative character of the metal. In other words, a greater per cent of the silver salt is oxygen salt than is the case with the sodium salt, and this is perhaps one very important reason why a higher per cent of O-ester is obtained from the silver salt than from the sodium salt. The rate of alkylation of the various salts in equimolecular quantity is a function of their dissociation. Only the urazole ions are alkylated. The fact that different ratios of O-ester to N-ester are obtained from different salts proves that the equilibrium

between the 2 tautomeric salts is an equilibrium between the molecular forms $C_2$ and $C_3$ and not between the ions $C$ and $C_1$. This is exactly in accordance with the results found by Dimroth[1] in his work on ethyl 1-phenyl-5-oxy-1,2,3-triazole-4-carboxylate, who proved that the equilibrium is between the molecular enol and keto forms and not between the ions. If only the ions $C$ and $C_1$ were in equilibrium we should get the same ratio of O-ester to N-ester from all the salts.

The fact that the ratio of O-ester to N-ester obtained from the potassium 1-phenyl-4-methylurazole is the same at 22°, 60° and 90° shows that the ratio of the molecular forms, $K_2$, does not change with the temperature. This is exactly what Dimroth found to be the case with the keto and enol forms of the ethyl 1-phenyl-5-oxy-1,2,3-triazole-4-carboxylate. The temperature coefficient of dissociation of the salts $C_2$ and $C_3$ is very small and nearly the same for all salts, as was proved by Jones and West[2] and by Noyes[3] and Coolidge.

The ratio of N-ester to O-ester, obtained from the silver salt in ether solution is 35:65, whereas the ratio obtained in 40 per cent alcohol-water is 41:59. This is due either to a change in the relative reactivity of the 2 ions towards ethyl iodide or to a change in the value of $K_2$ with change of solvent. That the first can be great is very improbable. But that the value of $K_2$ can, and probably will, change with the solvent is made almost certain by the work of Dimroth,[4] who showed that the ratio of the molecular enol and keto forms of ethyl 1-phenyl-5-oxy-1,2,3-triazole-4-carboxylate is 1:14 in water, 1:150 in methyl alcohol and 1:300 in ethyl alcohol. The theory proposed by the writer predicts a change in ratio of the 2 salts and the esters obtained with a change in solvent, as is found to be true experimentally. Indeed, if the proper solvents and experimental conditions were chosen both forms of the salts could probably be isolated. Apparently, Hantzsch[5] made 2 isomeric salts of cyanuric acid, Titherly[6] made isomeric silver salts of benzamide and acetamide,

[1] Ann. Chem. (Liebig), 338, 1; 338, 143.
[2] This Journal, 34, 357.
[3] Z. physik. Chem., 46, 323 (1904). J. Am. Chem. Soc., 26, 134 (1904).
[4] *Loc. cit.*
[5] Ber. d. chem. Ges., 35, 2717 (1902).
[6] J. Chem. Soc., 79, 409 (1901).

and Wislicenus[1] apparently had isomeric copper and sodium salts of formylphenylacetic ester.

The theory proposed predicts that, as Remsen and Hillyer[2] and Lengfeld[3] found, different alkyl halides will have different reaction coefficients, $K_3$ and $K_4$, and that the ratio of O-ester to N-ester obtained from a given salt may vary with different alkyl halides. This has been found true experimentally; whereas 0.3 N solution of potassium salt in 40 per cent alcohol-water containing equimolecular quantity of ethyl iodide reacted at 60° in 1 hour to the extent of 30.35 per cent, and 90 per cent of the reaction product was N-ester, the potassium salt and ethyl bromide, under exactly the same conditions, reacted to the extent of 22.5 per cent and 87.7 per cent of the reaction product was N-ester.

JOHNS HOPKINS UNIVERSITY,
June, 1906.

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**Contribution from the Texas Experiment Station.**

## A SIMPLE FAT EXTRACTION APPARATUS.[4]

BY G. S. FRAPS.

This is a mercury sealed apparatus, simple in construction, cheap and easy to operate. Several pieces of this apparatus have been in use in the Texas Experiment Station since the fall of 1905 and have given satisfactory results.

The apparatus is represented in the accompanying drawings. Fig. I. shows the apparatus set up ready for use. Fig. II. is the vessel used for extraction. It is fitted with a fat extraction cartridge. Fig. III. represents a flask which is similar to Knorr's flask. Fig. IV. is a condenser. The water enters A and leaves at B. The cork C should have openings made in it, otherwise the mercury may be thrown out of the flask when the extraction is begun. Fig. V. is a straight glass jacket, 1 inch in outside diameter. The two prongs at the

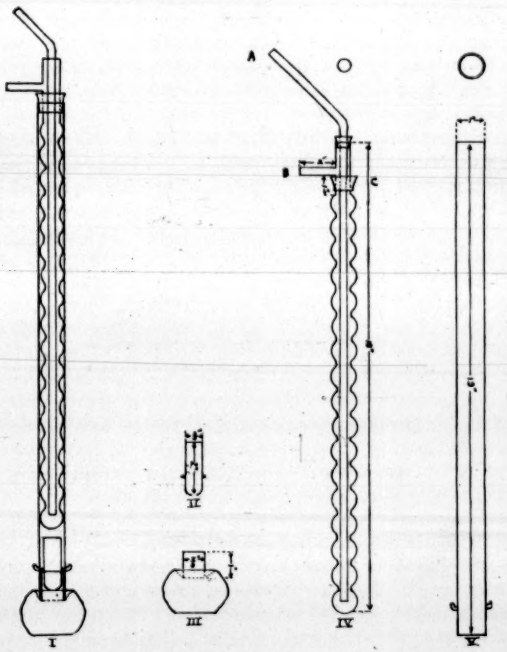
[1] Ann. Chem. (Liebig), **291**, 147.

[2] THIS JOURNAL, **8**, 251.

[3] *Ibid.*, **11**, 40.

[4] The apparatus has some points of resemblance to Knorr's, described in Wiley's "Principles and Practice of Agricultural Analysis," 1 Ed., Vol. III., pp. 44-47, but is much simpler, is only one-third as costly and any part may be replaced at slight expense.

lower end of the tube serve to hold the flask for the fat by means of rubber bands, if desired. We never employ them.




In using the apparatus the substance is placed in the tube and dried. It is then fitted in the neck of the flask, Fig. III, and the apparatus set up as shown in Fig. I. The depression in the flask is filled with mercury. The amount of ether required depends upon the atmospheric temperature. In cool weather a small quantity suffices for the extraction. The relative dimensions of the several pieces are shown in the

drawings. They can, of course, be modified very easily if desired. A siphon arrangement can be used in place of the capsule, Fig. II.; in such case the jacket, Fig. V., must be made a little longer.

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Contributions from the Chemical Laboratory of Harvard College.

## ON THE CONSTITUTION OF THE $\alpha$- AND $\beta$-ADDITION COMPOUNDS OF ALCOHOLS AND TETRABROMORTHOBENZOQUINONE.[1]

By C. Loring Jackson and R. D. MacLaurin.

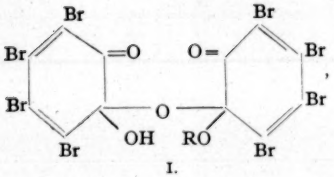
In 1904 Horace C. Porter and one of us[2] described 2 series of addition compounds formed by the union of tetrabromorthobenzoquinone with alcohols, the general formula for each of which was $(C_6Br_4O_2)_2.ROH$. The first ($\alpha$) series was formed by the direct action of the alcohols on the quinone in the cold. Its members were characterized by crystallizing in needles, which turned red on melting from the formation of hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$, and by conversion into the corresponding member of the $\beta$-series by boiling with a dilute solution of sodic hydrate, or, less conveniently, by the regulated action of acetic anhydride. We have found that the same change is brought about with the methyl compound by warming it with a mixture of benzene, hydroxylamine hydrochloride and sodic carbonate, and this seems to be an even better method of making this $\beta$-compound than that with sodic hydrate. The members of the $\beta$-series are characterized by crystallizing in rhombic plates, which melt to a colorless liquid, and by an unusual stability.

In the first paper[3] on this subject, reasons were given for reducing the possible structural formulas for the $\alpha$-alcohol compounds to two:

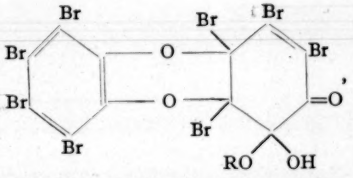
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Robert D. MacLaurin.

[2] This Journal, 31, 89 (1904).

[3] *Ibid.*, 31, 92 (1904).



I.



II.

which will be briefly recapitulated here. The 2 benzene rings cannot be united by the carbon atoms either of the rings themselves or of the added substance, as the compounds thus formed would be too stable to drop by mere heat into the hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$; they must therefore be united by the oxygen either directly, as in the above formulas, or with the added substance taking part in the union; this latter method of union must be rejected, because there is a water compound resembling the alcohol compounds most closely, and, if the union is effected through the quinone oxygen and the carbon of the alcohol, this water compound must have an entirely different structure from the alcohol bodies. If, on the other hand, all these substances have the same structure, which can hardly be doubted, and the added body takes part in the union, it must take place through chains of oxygen atoms, giving a structure much less stable than that of the *a*-compounds. The rejection of the second supposition—that the carbon of the alcohol takes part in the union—is supported by the observation that the benzyl alcohol compound gave no benzoic acid when decomposed with hydrobromic acid, whereas

this product must have been formed with such an arrangement of the molecule.

Neither in the paper by Porter (just cited) nor in that of Carlton,[1] nor of Russe,[2] was any convincing argument given for deciding whether Formula I. or II. was the correct one. Such an argument we have found in the conversion of an $\alpha$- into a $\beta$-compound by the regulated action of acetic anhydride, but before giving it we must discuss a change in Formula II., rendered necessary by our study of the action of sodic hydrate, in aqueous solution, on hexachlororthoquinopyrocatechin ether, which yielded hexachlordihydroxypyrocatechin ether and sodic chloranilate by the following reactions:

$$2C_6Cl_4O_2.C_6Cl_2O_2 + 6NaOH =$$

$$2C_6Cl_4O_2H_2 + 2C_6Cl_2O_2Na_2O_2 + 2NaOH =$$

$$C_6Cl_4O_2.C_6Cl_2O_2H_2 + 2NaCl + 2H_2O + 2C_6Cl_2O_2Na_2O_2.$$

That tetrachlorpyrocatechin is converted into hexachlordihydroxypyrocatechin ether by the action of a warm solution of sodic hydrate was proved by a special experiment.

That the sodium salt formed in this reaction is derived from chloranilic acid, and not from an isomeric dioxyortho- or paraquinone, was proved by a careful comparison of it[3] with chloranilic acid made from chloranil. This comparison may be divided into 3 parts:

1. The determination of the water of crystallization in the 2 acids and several of their salts with the following results:

$$C_6Cl_2(OH)_2O_2.2H_2O; \quad C_6Cl_2(OK)_2O_2.H_2O.$$

(The potassium salt from orthoquinone also crystallized with $2H_2O$.)

$$C_6Cl_2(ONa)_2O_2.3H_2O.$$

(Valeur[4] found that sodic chloranilate crystallizes at 35° with $4H_2O$, at ordinary temperatures with $3H_2O$. Six of our deter-

[1] THIS JOURNAL, **34**, 422 (1905).

[2] *Ibid.*, **35**, 154 (1906).

[3] For much of this comparative work the material was derived from tetrachlororthoquinone and methyl alcohol, instead of from the hexachlor ether.

[4] Ann. Chim. Phys., [7], **29**, 507.

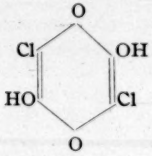
minations gave percentages for $3H_2O$, one gave an amount not far from $4H_2O$.)

$$C_6Cl_2O_2BaO_2.3H_2O.$$

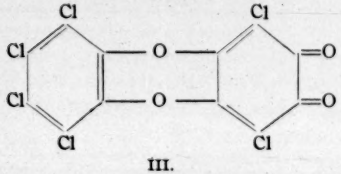
In every case the salt of the acid from the orthoquinone was identical in appearance with that from chloranil.

2. The behavior of the ammonium salts of the 2 acids was studied with a number of reagents. In each case the color of the precipitates was the same and, as many of these colors are very striking, this is a strong proof of their identity.

3. The silver salt of the acid from the orthoquinone was converted into the dimethyl ether by treatment with methyl iodide. This melted at 141°–142°, the melting point given by Kehrmann[1] for the 3,6-dichlor-2,5-dimethoxyquinone prepared from chloranilic acid. These comparisons leave no doubt that the second product of the action of sodic hydrate on hexachlororthoquinopyrocatechin ether is the sodium salt of chloranilic acid. Chloranilic acid has the constitution[2]



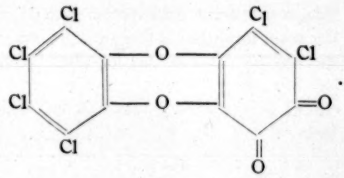

and it follows from this that the formula of the hexachlor ether must be symmetrical (III., not IV.).




III.

[1] J. prakt. Chem. [2], **40**, 370.

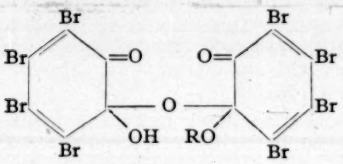
[2] Hantzsch: Ber. d. chem. Ges., **20**, 1303 (1887). Hantzsch and Schniter: *Ibid.*, **20**, 2280.



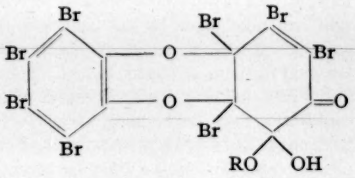
IV.

The hexabrom ether resembles the hexachlor so strongly in every respect that it must have a similar symmetrical structure, and this inference was confirmed by treating it with a warm solution of sodic hydrate, when sodic bromanilate was formed. This was identified by its properties and an analysis of the free acid, as more work did not seem worth while after the thorough identification of the chloranilic acid given above.

We now return to Formulas I. and II. for the alcohol addition compounds of the *a*-series.



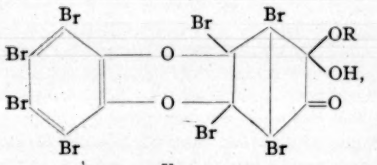
I.



II.

Formula II. owes its justification only to the fact that these *a*-bodies, when heated, pass easily into the hexabrom ether, $C_6Br_4O_2.C_6Br_2O_2$, but if this ether has the symmetrical structure

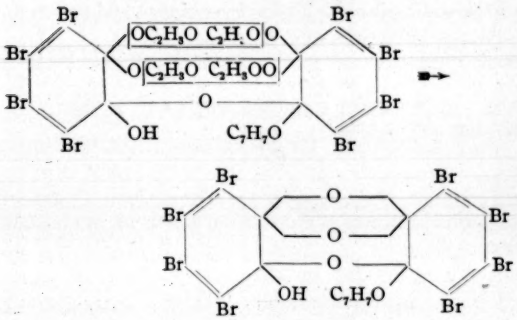
III., a substance constituted as in II. could pass into it only by the most improbable transformations, so that this formula must be rejected. If we try to save the principle embodied in II. by converting it into a symmetrical formula, we encounter difficulties in the arrangement of the bonds, as the only possible form, V.,




V.

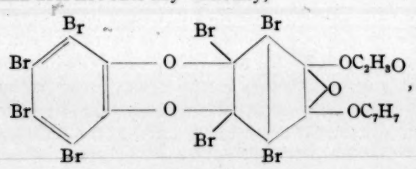
does not conform to Kekulé's theory of the benzene ring. But in spite of this it is not impossible, especially when the occurrence of para chains among the terpenes is remembered. On the other hand, a configuration such as this para bond, which does not come under the prevailing theory, or, in other words, which is not in harmony with most of the observed facts of the science, is certainly a strong, although not conclusive argument against the adoption of such a formula.

The proof that Formula V. is not correct rests on the formation of the $\beta$-benzyl compound, by the regulated action of acetic anhydride on the $\alpha$-body, which can be explained with Formula I., but is impossible with V. With Formula I. this action can take place by the addition of 2 molecules of acetic anhydride to the 2 quinone oxygen atoms, and the subsequent removal of them as shown below. Such an addition of acetic anhydride, followed by its removal without any change in the conditions, may be brought about by the natural tendency to form such a very stable product as the $\beta$-compound, or, if it is less soluble than the intermediate acetacetal, there would be nothing strange in its formation:




VI. *β*.

The formula (VI.) for the *β*-compounds, to which this course of reasoning leads, is certainly a strange one, but we have not succeeded in finding any other which will represent the formation of the free (not acet) *β*-compound by this reagent, and the other reactions for the formation of the *β*-compounds also lead naturally to this same formula. On the other hand, we cannot explain the conversion of the *α*- into the *β*-compound by acetic anhydride, if Formula V. is adopted. The formation of an acet compound does not offer any difficulty,




VII.

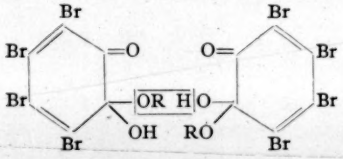
but actually the product is the hydroxy, not the acet compound, and the acet body, if formed at first, could not be converted into the hydroxy compound by the action of cold water, or methyl alcohol, or benzene (the only agents used with it in this case), since this acet body[1] has been made by the action of

[1] Jackson and Carlton: THIS JOURNAL, **34**, 440 (1905).

boiling acetic anhydride on the β-compound, and proved to be stable even with sodic hydrate.

The proof of the accuracy of Formula I., given in the preceding paragraph, is supported by the 2 following arguments, which, by themselves, are almost sufficient to establish the constitution of these bodies.

The formation of the α-compound by the action of the alcohol on the quinone in the cold can be explained according to Formula I., as follows: The quinone is first converted into a hemiacetal, and then 2 molecules of this split out a molecule of the alcohol, thus:




These reactions suppose an addition of the alcohol followed by a removal of it without any change in the conditions, as in the case just discussed, but, if the α-body is much less soluble than the hypothetical hemiacetal, there is nothing strange in this supposition. On the other hand, the formation of a substance having Formula V. is inexplicable. Why should the presence of an alcohol, whether it form a hemiacetal or not, cause the opening of a double bond and the addition of $C_6Br_4O_2$ to the benzene ring? The formation of such a compound shows, it is true, a certain analogy to the formation of quinhydrones, but this rather tells against this formula than its favor, as all quinhydrones known are strongly colored (the octobromorthoquinhydrone being black[1]), so that the white or yellowish-white α-bodies can hardly be related to them.

The β-compounds melt without decomposition and show a very slight tendency to give up bromine with reagents. For instance, the β-methyl compound showed no sign of decomposition after being boiled with an alcoholic solution of sodic ethylate for an hour, whereas tetrabromorthoquinone was at-

[1] Jackson and Russe: THIS JOURNAL, 35, 176 (1906).

tacked at once. This striking stability is explained by Formula VI. derived from I., but not by any expression we have been able to derive from Formula V., as it does not seem possible that 2 atoms of bromine[1] could be held firmly, when exposed to the loosening action of oxygen attached to the same carbon and of acetal groups in the para position, especially when the similar atoms of bromine in the *a*-body (V.) are easily removed by the action of heat. It is true that the quino and hemiacetal groups of the *a*-body (V.) have been converted into hemiacetal and acetal groups in the *β*-, but, although this would diminish their loosening effect on the bromine, it is not possible that it would entirely destroy it, and even fix these atoms of bromine more firmly than in the tetrabromorthoquinone.

The one reaction of these substances, which is explained better by V. than by I., is the conversion of the *a*-compound into hexabromorthoquinopyrocatechin ether by heat. If I. is the true formula, the molecule must split into 2 molecules of tetrabromorthoquinone and 1 of the alcohol, which then, by the loss of 2 atoms of bromine and the alcohol, give the hexabrom ether. That tetrabromorthoquinone is converted by heat into the hexabrom ether, $C_6Br_4O_2.C_6Br_2O_2$, has been determined by a special experiment,[2] which we have verified more recently. The ether obtained in this case is less pure than that from the action of heat on an *a*-compound, but this is undoubtedly explained by the effect of the alcohol in the latter case, which would promote the formation of the ether by converting part of the tetrabromorthoquinone into tetrabrompyrocatechin.

For greater clearness we add a brief recapitulation of our reasons for rejecting Formula V., thus proving that Formulas I. and VI. are those of the *a*- and *β*-compounds. (1) The regulated action of acetic anhydride converts the *a*-benzyl compound into the free (not acet) *β*-compound. Formula V. could give only the acet *β*-compound under these conditions. (2) Formula V. is not in harmony with Kekulé's theory of the benzene

[1] The hydroxyl compound corresponding to Formula VII. shows the position of these 2 atoms of bromine.

[2] Jackson and Porter: THIS JOURNAL, 31, 118 (1904).

ring. (3) The formation of a substance with Formula V. from an alcohol and tetrabromorthoquinone is inexplicable. (4) The β-compound derived from Formula V. must be an unstable substance. As a matter of fact, the β-compounds are remarkably stable. According to Formulas I. and VI. the names of the methyl compounds would be, for the α-body octobromorthoquino-1-methoxy-1′-hydroxy-1-monoxide; for the β-compound, octobromorthoquino-1-methoxy-1′-hydroxy-1,2,2-trioxide.

Since the symmetrical structure of the hexabromorthoquinopyrocatechin ether has been established, it follows that Shaffer's[1] addition compound,

$$C_6Br_4O_2.C_6Br_2O_2.(CH_3OH)_2,$$

and the heptabromhemiether of Russe,[2]

$$C_6Br_4OHO.C_6Br_3O_2,$$

must also have a symmetrical structure.

Some preliminary experiments are also described in the body of the paper, which have given promising results.

## EXPERIMENTAL.

### *Action of Sodic Hydrate on Hexachlororthoquinopyrocatechin Ether.*

If a 10 per cent solution of sodic hydrate was added to the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, in quantity, there was formed almost immediately a deposit of purplish-black, short, stout needles, which seemed to be an addition compound of the ether and sodic hydrate, as dilute sulphuric acid regenerated the ether and an analysis of the crystals, with no other purification than washing with water, gave 3.98 per cent of sodium, which is not very far from 4.98, the amount of sodium in $C_{12}Cl_6O_3.NaOH$. If, on the other hand, the sodic hydrate was added gradually, a different result was obtained. For this purpose 2 grams of hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, were warmed with 50 cc. of water in an evaporating dish on the steam-bath and single drops of a 10 per

[1] THIS JOURNAL, 34, 460 (1905).
[2] *Ibid.*, 35, 156 (1906).

cent solution of sodic hydrate added at frequent intervals. A reaction began after the addition of a few drops and was brought to an end by continuing the heating and addition of sodic hydrate for an hour. The total quantity of sodic hydrate used, however, did not exceed 30 drops. The products of the reaction were hexachlordihydroxypyrocatechin ether, identified by its brown color, melting point of 290°, and conversion by nitric acid into the red orthoquino ether, $C_6Cl_4O_2.C_6Cl_2O_2$, and sodic chloranilate, recognized by its color, crystalline form, and the following analysis of the salt purified by 2 recrystallizations from water.

0.3456 gram of the air-dried salt lost, at 110°, 0.0614 gram $H_2O$ and gave 0.1597 gram of $Na_2SO_4$.

| | Calculated for $C_6Cl_2(ONa)_2O_2.3H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 17.59 | 17.76 |
| | **Calculated for $C_6Cl_2(ONa)_2O_2$.** | **Found.** |
| Na | 18.19 | 18.20 |

In the reaction described above the hexachlordihydroxypyrocatechin ether must have been formed from the tetrachlorpyrocatechin resulting with the sodic chloranilate from the decomposition of the orthoquino ether. It seemed important, therefore, to determine whether tetrachlorpyrocatechin underwent such a reaction in presence of sodic hydrate. Accordingly, 1 gram of tetrachlorpyrocatechin was warmed on the steam-bath with dilute sodic hydrate, and in the course of a few minutes chocolate-brown needles appeared, which showed the melting point, 290°, of the hexachlordihydroxy ether and were converted by nitric acid, quantitatively, into the orthoquino ether. There can be no doubt, therefore, that they were this substance.

As one of the most important arguments in regard to the constitution of our orthoquinone derivatives is based on this formation of chloranilic acid, we give the proof that our product was this substance and not an isomeric dihydroxyquinone. It was first encountered as one of the products of the action of methyl alcohol on tetrachlororthoquinone, and in the beginning

we hoped it might be a dihydroxyorthoquinone, which must be the immediate product of the reaction either with methyl alcohol or sodic hydrate. To establish its identity we analyzed the acid and a number of its salts, and for the sake of absolute certainty, made parallel analyses of the corresponding compounds derived from chloranil in the usual way.

Chloranilic acid from chloranil and the substance from tetrachlororthoquinone and methyl alcohol, or the red ether and sodic hydrate, crystallized from water in reddish brown, hexagonal plates, which sublimed in open tubes without melting, and with water gave the characteristic purple solution. They were dried on filter paper for analysis. In these analyses the substance from orthoquinone will be called *a*, that from chloranil *b*.

I. 0.2350 gram substance *a*, when heated to 110°, lost 0.0343 gram $H_2O$.

II. 0.3580 gram substance *a* lost 0.0512 gram $H_2O$.

III. 0.4226 gram substance *b* lost 0.0593 gram $H_2O$.

IV. 0.3027 gram substance *b* lost 0.0426 gram $H_2O$.

| | Calculated for $C_6Cl_2(OH)_2O_2.2H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| | | *a.* | | *b.* | |
| $H_2O$ | 14.69 | 14.60 | 14.30 | 14.04 | 14.07 |

In experiment II. it was found that 13.91 per cent of the water went off by drying in the air. Both substances sublimed without melting in open tubes and gave the characteristic purple solution with water.

The dark, purplish-red needles of the potassium salt, after crystallization from water, were dried *in vacuo*.

I. 0.1342 gram substance *a*, when heated to 110°, lost 0.0085 gram $H_2O$.

II. 0.1994 gram substance *a* lost 0.0118 gram $H_2O$.

III. 0.3582 gram substance *b* lost 0.0215 gram $H_2O$.

IV. 0.2456 gram substance *b* lost 0.0143 gram $H_2O$.

V. 0.1023 gram substance *a* gave 0.0976 gram AgCl.

| | Calculated for $C_6Cl_2(OK)_2O_2.H_2O$. | Found. I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|---|
| | | *a.* | | *b.* | | *a.* |
| $H_2O$ | 5.94 | 6.33 | 5.92 | 5.95 | 5.82 | . . |
| Cl | 23.43 | . . | . . | . . | . . | 23.59 |

I. 0.1876 gram substance *a*, dried at 110°, gave 0.1143 gram $K_2SO_4$.

II. 0.3369 gram substance *b* gave 0.2046 gram $K_2SO_4$.

| | Calculated for $C_6Cl_2(OK)_2O_2$. | Found. I. *a*. | II. *b*. |
|---|---|---|---|
| K | 27.44 | 27.35 | 27.27 |

The salt from tetrachlororthoquinone was also observed with 2 molecules of water.

I. 0.3027 gram salt *a*, dried *in vacuo*, when heated to 110°, lost 0.0335 gram $H_2O$.

II. 0.2096 gram salt *a* lost 0.0225 gram $H_2O$.

III. 0.2304 gram salt *a*, dried *in vacuo*, gave 0.1267 gram $K_2SO_4$.

IV. 0.2278 gram salt *a* gave 0.2070 gram AgCl.

| | Calculated for $C_6Cl_2(OK)_2O_2.2H_2O$. | Found. I. | II. | III. *a*. | IV. |
|---|---|---|---|---|---|
| $H_2O$ | 11.20 | 11.06 | 10.73 | . . | . . |
| K | 24.34 | . . | . . | 24.64 | . . |
| Cl | 22.12 | . . | . . | . . | 22.47 |

0.1871 gram salt *a*, dried at 110°, gave 0.1132 gram $K_2SO_4$.

| | Calculated for $C_6Cl_2(OK)_2O_2$. | Found. *a*. |
|---|---|---|
| K | 27.44 | 27.17 |

Probably the potassium salt from chloranil could also have been obtained with 2 molecules of water, but we did not think it worth while to search for this combination.

The dark red needles of the sodium salt were dried in the air for analysis:

I. 0.4432 gram salt *a*, dried at 110°, lost 0.0789 gram $H_2O$.

II. 0.3472 gram salt *a* lost 0.0631 gram $H_2O$.

III. 0.2555 gram salt *a* lost 0.0470 gram $H_2O$.

IV. 0.2509 gram salt *a* lost 0.0541 gram $H_2O$.

V. 0.2409 gram salt *b* lost 0.0419 gram $H_2O$.

VI. 0.2801 gram salt *b* lost 0.0503 gram $H_2O$.

| | Calculated for $C_6Cl_2(ONa)_2O_2.3H_2O$. | Found. I. | II. *a*. | III. | IV. | V. *b*. | VI. |
|---|---|---|---|---|---|---|---|
| $H_2O$ | 17.59 | 17.80 | 18.18 | 18.39 | 21.57 | 17.39 | 17.95 |

Valeur[1] obtained the sodic chloranilate at ordinary temperatures with $3H_2O$, at 35° with $4H_2O$. Our 6 determinations, all but IV., agree with the salt with $3H_2O$. IV. approaches the percentage required by $4H_2O$, which is 22.15.

I. 0.3643 gram salt *a*, dried at 110, gave 0.2047 gram $Na_2SO_4$.

II. 0.2298 gram salt *b* gave 0.1283 gram $Na_2SO_4$.

| | Calculated for $C_6Cl_2(ONa)_2O_2$. | Found. I. *a*. | II. *b*. |
|---|---|---|---|
| Na | 18.19 | 18.20 | 18.09 |

The fawn-colored barium salt, purified by washing with hot distilled water, was dried in the air for analysis:

I. 0.2395 gram salt *a*, air-dried, lost at 110°, 0.0329 gram $H_2O$.

II. 0.2404 gram salt *a* lost 0.0339 gram $H_2O$.

III. 0.2859 gram salt *b* lost 0.0376 gram $H_2O$.

IV. 0.3694 gram salt *b* lost 0.0497 gram $H_2O$.

| | Calculated for $C_6Cl_2O_2BaO_2.3H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| | | *a*. | | *b*. | |
| $H_2O$ | 13.58 | 13.74 | 14.10 | 13.15 | 13.46 |

I. 0.2066 gram salt *a*, dried at 110°, gave 0.1395 gram $BaSO_4$.

II. 0.2483 gram salt *b* gave 0.1679 gram $BaSO_4$.

| | Calculated for $C_6Cl_2O_2BaO_2$. | Found. I. *a*. | II. *b*. |
|---|---|---|---|
| Ba | 39.82 | 39.69 | 39.76 |

The behavior of dilute ammoniacal solutions of the 2 substances with various reagents was found to be identical, giving the following striking reactions with salts of the metals named:

Barium, Strontium, brown precipitate.
Magnesium, brown needles with tapering ends.
Zinc, pinkish white.
Cadmium, yellowish brown.
Cobalt, groups of pale purple needles.
Nickel, grass-green precipitate.
Lead, fawn color.
Copper, bluish green.

[1] Ann. Chim. Phys., [7], **29**, 507.

Bismuth, dark blue.

Silver, dark brown, fern-shaped crystals.

Finally, the substance from tetrachlororthoquinone was converted into its dimethyl ether by adding argentic nitrate to a dilute ammoniacal solution of it and heating the dry, brown silver salt to 100° with the calculated quantity of methyl iodide, in a sealed tube, for 2 hours. The product, after crystallization from hot benzene, melted at 141°–142°, the melting point of the 3,6-dichlor-2,5-dimethoxyparaquinone, according to Kehrmann.[1] There can be no doubt, therefore, that the substance obtained from haxachlororthoquinopyrocatechin ether and sodic hydrate, or from tetrachlororthoquinone by the action of methyl alcohol is chloranilic acid, which must have been formed from the dihydroxyorthoquinone—the first product of the reaction—by the familiar shifting from an oxyorthoquinone to a derivative of the para series.

*Formation of Bromanilic Acid from Hexabromorthoquinopyrocatechin Ether.*

Two grams of the hexabromorthoquinopyrocatechin ether were allowed to stand with a dilute solution of sodic hydrate over night, when long, purplish red needles were deposited. These were acidified with dilute sulphuric acid, recrystallized from water twice and dried for analysis:

0.1823 gram substance gave 0.2302 gram AgBr.

| | Calculated for $C_6Br_2(OH)_2O_2$. | Found. |
|---|---|---|
| Br | 53.69 | 53.73 |

The substance was recognized as bromanilic acid by its color and crystalline form, the purple solution which it formed with water, and the nearly black prisms of the sodium salt.

*Action of Heat on Tetrabromorthoquinone.*

Porter[2] found that when tetrabromorthoquinone was heated bromine was given off and hexabromorthoquinopyrocatechin ether formed, but the ether made in this way contained a white impurity, which was not further studied. We have repeated

[1] J. prakt. Chem., [2], 40, 370.

[2] THIS JOURNAL, 31, 118 (1904).

this experiment and obtained the ether, and have also tried the action of heat on tetrachlororthoquinone, which gives the hexachlor ether even more easily.

*Behavior of the β-Addition Compound, Octobromorthoquino-1-methoxy-1′-hydroxy-1-2,2-trioxide with Sodic Ethylate.*

When the β-compound, $(C_6Br_4O_2)_2.CH_3OH$, was heated with a strong alcoholic solution of sodic ethylate, during the first hour there was no visible action, but after the mixture had been heated 10 hours, dark-colored products were formed and tests obtained for bromide and pyrocatechin. The β-compound is, therefore, much less easily affected by sodic hydrate than tetrabrompyrocatechin, which reacts with it at once, somewhat even in the cold, very readily when heated.

The β-addition compound, $(C_6Br_4O_2)_2.CH_3OH$, when heated with amyl alcohol and metallic sodium, seemed to be completely decomposed in about 10 minutes. Tests were obtained for bromide and pyrocatechin.

*Action of Hydroxylamine on the α-Addition Compound, Octobromorthoquino-1-methoxy-1′-hydroxy-1-monoxide.*

One gram of the addition compound was dissolved in benzene and mixed with the hydrochloride of hydroxylamine and sodic carbonate. Upon warming the mixture on the steam-bath, glistening white leaflets began to separate almost immediately, which were filtered out and washed with water, when they were found to melt at 259°–260°. One crystallization from a mixture of equal parts of benzene and chloroform raised the melting point to 261°–262°, when the substance was dried and analyzed:

0.2398 gram substance gave 0.4094 gram AgBr.

| | Calculated for $(C_6Br_4O_2)_2.CH_3OH$. | Found. |
|---|---|---|
| Br | 72.73 | 72.64 |

As the substance crystallizes in white rhombic plates and melts at 261°–262° to a colorless liquid, there can be no doubt that it is the β-methyl alcohol compound. This seems to be a remarkably good way of making this substance, as the yield is quantitative and the product essentially pure.

The following experiments were tried in the hope of getting new data for the determination of the constitution of the *a*-bodies. In no case did they go beyond the preliminary stage, and it must be understood, therefore, that all the results are subject to revision.

*Action of Acetic Anhydride on the a-Methyl Compound*, $(C_6Br_4O_2)_2.CH_3OH$.—Two grams of the *a*-methyl compound were shaken with 15–20 cc. of acetic anhydride for 15 minutes and then allowed to stand at ordinary temperatures for several hours, when it was found that the solid had turned yellow. This product was filtered out, washed with ligroin and recrystallized 4 times from a mixture of equal parts of benzene and ligroin, when it showed the constant melting point 225°.

0.1941 gram substance gave 0.3321 gram AgBr.

| | Calculated for $(C_6Br_4O_2)_2.CH_3OH$. | Found. |
|---|---|---|
| Br | 72.73 | 72.81 |

If this is not a mixture of the *a*- and *β*-isomers but a definite compound, it is the first representative of a new—*γ*—class of bodies, as it melts at 225°, whereas the *a*-body melts at 178°–182°, the *β*-compound at 261°. That the substance is not such a mixture is indicated by the following observations: Its yellow color, its constant melting point, the formation of a brownish-red substance on melting instead of the bright red given by the *a*-compounds, the fact that it crystallizes in needles from ligroin, and in clustered plates from benzene and ligroin, whereas the plates of the *β*-compound do not occur in clusters, and its greater solubility in organic solvents.

*Properties.*—It crystallizes in clusters of yellow plates, which turn brownish-red and melt at 225°. It is easily soluble in ethyl or methyl alcohol, ether, acetone, ethyl acetate, benzene, or toluene; slightly soluble in ligroin. Strong sulphuric acid has no effect on it in the cold and only a slight one when hot. Neither strong nitric acid nor strong hydrochloric acid acts on it. Sodic hydrate dissolves it and the solution gives a white precipitate with dilute sulphuric acid. Ammonic hydrate turns it white and dissolves it slightly.

A white product, melting with reddening at 218°, was also formed in the reaction described above, but we can say nothing about its composition.

By the action of warm acetic anhydride a white product, melting at 138°–140°, and by longer action one melting and reddening at 195°, and, finally, hexabromorthoquinopyrocatechin ether were formed.

The object of this work was to isolate some of the intermediate products formed in the conversion of the *α*- into the *β*-compound. While the substance analyzed does not seem to be one of these, it is possible that some of the others may be the compounds sought; the examination of them will, therefore, be continued in this laboratory.

*Action of Acetic Anhydride on the α-Water Compound,* $(C_6Br_4O_2)_2.H_2O$.—This work was taken up in order to prepare and analyze the *β*-water body, which Porter[1] thought he had made, but, as no analysis was attempted, its nature was inferred from its properties, especially the facts that it crystallized in rhombic plates and melted at 221°–222° without visible decomposition. Our first experiments were tried with small quantities of acetic anhydride and sodic acetate, according to the directions of Porter, but as they gave principally the ether, $C_6Br_4O_2.C_6Br_2O_2$, we modified the conditions as follows: Two grams of the *α*-water compound were treated with enough acetic anhydride for complete solution, dried sodic acetate was then added and the mixture warmed on the steam-bath for 15–20 minutes, when only a small amount of the red ether was formed; 800 cc. of water were now added and the pale purple solution heated on the steam-bath until a white precipitate was thrown down, which was filtered off and recrystallized from a mixture of methyl alcohol and benzene, until it showed the constant melting point 240°, when it was dried for analysis:

I. 0.1807 gram substance gave 0.3234 gram AgBr.

II. 0.1711 gram substance gave 0.3096 gram AgBr.

III. 0.1899 gram substance gave 0.1284 gram $CO_2$ and 0.0424 gram $H_2O$.

[1] THIS JOURNAL, 31, 110 (1904).

| | Calculated for $C_{12}Br_8O_3$. | Calculated for $C_{12}Br_8O_4$. | Found. I. | Found. II. | Found. III. |
|---|---|---|---|---|---|
| Br | 76.92 | 75.48 | 76.15 | 77.03 | . . |
| C | 17.31 | 16.98 | . . | . . | 18.45 |
| H | . . | . . | . . | . . | 2.48 |

From the analyses alone the preference must be given to the formula $C_{12}Br_8O_3$, but we are inclined to think that its real formula is $C_{12}Br_8O_4$, because we cannot see how a substance containing $O_3$ could be formed from the *a*-compound, whereas the second formula would be the natural result of the complete application of the reaction by which *β*-compounds are formed from *a*-bodies. This point can be settled only by more analytical work.

Our substance is probably different from that obtained by Porter, as it melts at 240° instead of 221°–222°. It may well be that Porter's substance was the *β*-water compound, of which this is the anhydride. We hope that this interesting substance will be submitted to a thorough study in this laboratory in the near future.

*Properties.*—It crystallizes in white, polygonal plates, which melt at 240° without change of color. It is soluble in benzene; slightly soluble in acetone, ethyl acetate or toluene; essentially insoluble in alcohol or ligroin. The best solvent for it is a mixture of benzene and methyl alcohol. Cold, strong sulphuric acid has no effect on it, but when hot a faint reddish-brown solution is obtained. Strong nitric acid, strong hydrochloric acid, or sodic hydrate has no effect on it, hot or cold. Acetic anhydride has no further action on this substance, which is in accord with the formula $C_{12}Br_8O_4$.

Oxidizing agents, as a rule, have but little action on the *β*-compounds,[1] and in confirmation of this fact we found the methyl compound entirely unaltered by bromine and water. Hot, fuming nitric acid, on the other hand, acts upon it, giving, under carefully regulated conditions, a yellow oil and oxalic acid. In the cold, substances melting at 275°–280°, 230°, 100°–102° and oxalic acid were obtained. When the corresponding *β*-chlor compound, $(C_8Cl_4O_2)_2.CH_3OH$, was treated with fuming nitric acid it behaved in a similar way, giving a

[1] This Journal, 34, 441 (1905).

yellow oil and oxalic acid. The yields of all these bodies were so exceedingly small that the investigation of them will be very laborious.

Phenylhydrazine acted on the *a*-methyl body,

$$(C_6Br_4O_2)_2.CH_3OH,$$

even when gently warmed in alcoholic solution with it. In different experiments 2 products were obtained, one melting at 155°–156°, the other constant at 200°. Analyses of this latter product gave Br 36.20; N 15.49, 15.48; C 31.68; H 6.98; but we are unable to derive any formula from these percentages, as the number of atoms of carbon is only little more than twice the number of atoms of nitrogen. The substance, apparently, gives up phenylhydrazine easily to alkalies or acids.

Phenylhydrazine acts readily with the *β*-methyl compound, $(C_6Br_4O_2)_2.CH_3OH$, even when diluted with alcohol, which is strange in view of the marked stability of this compound toward other reagents, especially aniline. In the preliminary experiments 3 different products were obtained, one melting at 225° and giving Br 5.05; N 17.1 per cent; another melting at 162° and giving a test for halogen; and a third (made by the action of undiluted phenylhydrazine), which was free from halogen. Pyridine also acts on this *β*-compound, giving a brown product.

CAMBRIDGE, MASS.,
October 8, 1906.

## NOTE.

### *Dry Method for the Generation of Oxygen from Sodium Peroxide.*

The action of water on fused sodium peroxide is one of the most convenient and elegant methods for the preparation of oxygen for laboratory or lecture purposes. The liberation of the gas is so lively, however, that a specially constructed generator is usually required to enable one to control the evolution of it. To prepare a small quantity, the most efficient method is the decomposition of the substance by means of water of crystallization. A mixture of equal parts of fused sodium peroxide and crystallized sodium sulphate or carbonate, upon being gently warmed, evolves oxygen in a steady stream, under perfect control of the operator. A 10 gram piece of

"oxone" readily evolves, by this process, 4 liters of oxygen. The oxygen is 99 per cent pure, perfectly odorless, tasteless and colorless.

Within the last few months calcium carbide has been decomposed by a like process, known as the Atkins system, with the production of the so-called "sun gas," which is being developed by the Sun Gas Company, of London.

HAROLD J. TURNER.

## REPORTS.

### *Thiophosphoric Acids and Thiophosphates.*

Professor Alfred Stock and his assistants in the University of Berlin, published an article recently of which the following is an abstract.[1]

Stock and Hoffmann, 3 years ago, found that phosphorus pentasulphide dissolves in liquid ammonia, forming a yellow solution which becomes colorless on standing and deposits crystals of triammonium imidotrithiophosphate, (2) while diammonium nitrilodithiophosphate, (3) remains in solution in the liquid ammonia and can be isolated by evaporation in a vacuum; the numbers in parentheses refer to the structural formulas given in the table. The authors believe that the yellow solution of phosphorus pentasulphide in ammonia contains the ammonium salt of diimidothiopyrophosphoric acid, to which they assign the constitution (1). If so, the reaction is

$$P_2S_5 + 6NH_3 = (NH)_2P_2S_5(NH_4)_4$$

and this salt reacts with ammonia as follows:

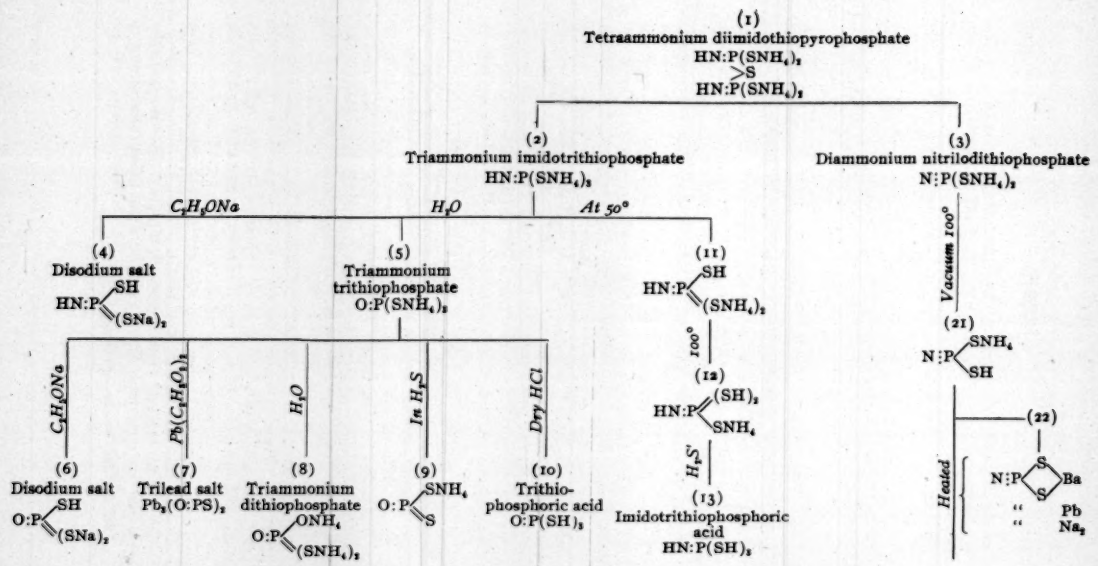
$$(NH)_2P_2S_5(NH_4)_4 + NH_3 = HNP(SNH_4)_3 + NP(SNH_4)_2.$$

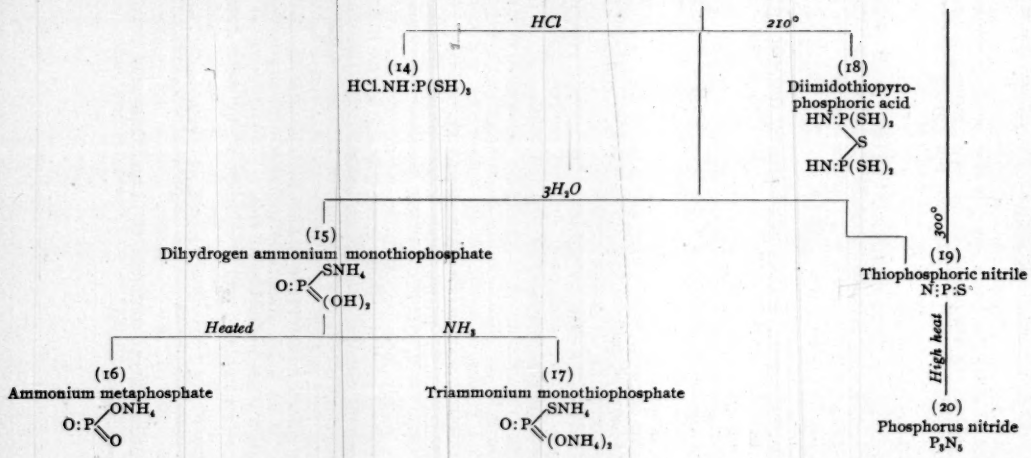
From these compounds the authors have isolated a number of derivatives. The limits of a report forbid dwelling on the experimental difficulties encountered; owing to the extreme ease with which the compounds are decomposed by water the work was arduous.

The ammonium imidotrithiophosphate (2) yields several products. Treated with sodium ethylate the disodium salt (4) is formed even when a large excess of sodium ethylate is used, the presence of the imide group apparently weakening the acid; the triammonium salt also is only stable at low temperatures, breaking down, at the ordinary temperature, into ammonia and the diammonium salt.

The ammonium imidotrithiophosphate is remarkably sensitive to moisture; when shaken with ether containing 1

[1] Ber. d. chem. Ges., 39, 1967 (1906).


(1)
Tetraammonium diimidothiopyrophosphate
HN:P(SNH4)2
>S
HN:P(SNH4)2
(2)
Triammonium imidotrithiophosphate
HN:P(SNH4)3
(3)
Diammonium nitrilodithiophosphate
N:P(SNH4)3
C2H5ONa
H2O
At 50°
Vacuum 100°
(4)
Disodium salt
HN:P
SH
(SNa)2
(5)
Triammonium trithiophosphate
O:P(SNH4)3
(11)
HN:P
SH
(SNH4)2
100°
(12)
HN:P
(SH)2
SNH4
H2S'
(13)
Imidotrithiophosphoric acid
HN:P(SH)2
(21)
N:P
SNH4
SH
(22)
Heated
N:P
S
S
Ba
"
Pb
"
Na2
C2H5ONa
Pb(C2H5O)2
H2O
In H2S
Dry HCl
(6)
Disodium salt
O:P
SH
(SNa)2
(7)
Trilead salt
Pb3(O:PS)2
(8)
Triammonium dithiophosphate
O:P
ONH4
(SNH4)2
(9)
O:P
SNH4
S
(10)
Trithiophosphoric acid
O:P(SH)3


HCl
210°
(14)
HCl.NH:P(SH)3
(18)
Diimidothiopyro-
phosphoric acid
HN:P(SH)2
S
HN:P(SH)2
3H2O
300°
(15)
Dihydrogen ammonium monothiophosphate
O:P
SNH4
(OH)2
(19)
Thiophosphoric nitrile
N:P:S
Heated
NH3
High heat
(16)
Ammonium metaphosphate
O:P
ONH4
O
(17)
Triammonium monothiophosphate
O:P
SNH4
(ONH4)2
(20)
Phosphorus nitride
P3N5

per cent of water the imide group is eliminated as ammonia, and is replaced by the oxygen of the water, forming triammonium trithiophosphate (5). Loss of the imide group strengthens the acid, for this triammonium salt does not lose ammonia at the ordinary temperature.

Triammonium trithiophosphate, treated with sodium ethylate, yields an extremely unstable disodium salt (6). A yellow trilead salt (7) and a white tricadmium salt were also made, the two latter being insoluble in water and relatively stable.

While the aqueous solution of ammonium trithiophosphate is not immediately decomposed, after standing a short time the water reacts, substituting oxygen for one sulphur atom which is thrown off as hydrogen sulphide. Triammonium dithiophosphate (8) results, which can be obtained in crystalline form by precipitation with alcohol from the aqueous solution. This substance has been already made by Kubierschky[1] by the action of phosphorus pentasulphide on aqueous ammonia; he made several salts of this acid. His work was repeated and confirmed by the present authors.

If triammonium dithiophosphate is heated in a current of hydrogen sulphide ammonium sulphide escapes and yellow ammonium dithiometaphosphate (9) is formed.

If the triammonium dithiophosphate is treated with dry, liquefied hydrogen chloride or hydrogen bromide, the free thio acid (10) is formed, but Stock did not succeed in obtaining this extremely unstable substance in a pure condition.

Returning to the triammonium imidotrithiophosphate (2), Stock found that if it were placed in a desiccator over sulphuric acid it readily loses one molecule of ammonia, forming the diammonium salt (11), which, at 100°, loses a second molecule of ammonia, forming the monammonium salt (12). When this latter salt is heated in a current of hydrogen sulphide, it loses the final molecule of ammonia and the yellow imidotrithiophosphoric acid (13) is obtained. This acid is very reactive; as an imido compound it forms, with dry hydrogen chloride, a white hydrochloride (14).

Imidothiophosphoric acid is decomposed by water forming ammonium trithiophosphate, $HNP(SH)_3 + H_2O = O:P\begin{matrix}SNH_4\\ \\ SH\end{matrix}$ . The decomposition continues till ammonium monothiophos-

[1] J. prakt. Chem., 1885, p. 93.

phate (15) is formed, which was isolated in a condition of purity,

$$HN:P(SH)_3 + 3H_2O = O:P(SNH_4)(OH)(OH) + 2H_2S.$$

Ammonium monothiophosphate when heated gives off hydrogen sulphide, leaving ammonium metaphosphate (16).

Ammonium monothiophosphate, if treated with liquid ammonia, yields the tertiary salt (17) which, like the corresponding phosphate, $(NH_4)_3PO_4$, is stable only in presence of ammonia.

Stock has succeeded in isolating the triammonium salts of the 3 thiophosphoric acids (5, 8, 17).

On heating imidotrithiophosphoric acid, hydrogen sulphide escapes. Probably several successive products are formed, but their isolation is difficult; the first of these, the pyro-acid (18) was, however, separated in a nearly pure condition. It is interesting because its ammonium salt is believed to be the substance formed by dissolving phosphorus pentasulphide in liquid ammonia (1). This belief found support in the behavior of the pyro-acid towards liquid ammonia; the acid dissolved, forming a yellow solution which behaved like the substance numbered (1).

If the imidotrithiophosphoric acid is heated in a vacuum at 300° it becomes colorless and loses still more hydrogen sulphide, forming thiophosphoric nitrile, of the empirical composition NPS (19). This substance has no acid properties and is not decomposed by water. It corresponds to the known phosphoric nitrile NPO.

When the nitrile is heated to redness there remains the phosphorus nitride, $P_3N_5$: $5PNS = P_3N_5 + P_2S_5$.

This nitride was discovered by Stock and Hoffmann some time ago. Stock and Grüneberg are now engaged in experimenting on its direct formation from phosphorus pentasulphide and ammonia. They have observed that if phosphorus pentasulphide is treated at ordinary temperatures with dry, gaseous ammonia and gradually heated to 850°, all of the phosphorus of the pentasulphide is found as nitride. This could be expressed by the empirical equation:

$$3P_2S_5 + 10NH_3 = 2P_3N_5 + 15H_2S.$$

But few derivatives were obtained from the diammonium nitrilodithiophosphate (3). It is an amorphous, colorless substance; heated in a vacuum at 100° it loses ammonia, leaving the crystalline monammonium salt (21) from which the barium, lead and disodium salts (22) were prepared.

When the ammonium nitrilodithiophosphate is heated in a vacuum, it loses ammonia and hydrogen sulphide. Numerous attempts to isolate the free nitrilothio-acid failed. If the heat was raised to 300° the thionitrile, NPS (19), was obtained, while if red heat was employed the nitride, $P_3N_5$, was the endproduct.

Other sulphides of phosphorus react with liquid ammonia, but apparently in a more complicated manner.

E. RENOUF.

*On a Method for Determining the Specific Heat of Solutions; Contribution to the Study of Hydrates.*

In a recently published paper[1] Fuchs describes a simple and accurate method for the study of the specific heats of solutions, and shows how the hydrates existing in these solutions affect the results.

The same amount of energy was imparted at the same rate to the different solutions, by passing a measured current of electricity through a glass tube containing mercury, which was completely immersed in the liquid that was being investigated. This liquid was contained in a platinum calorimeter of 600 cc. capacity, so arranged that it might be surrounded by a constant temperature bath. The usual precautions were taken to obtain uniform temperature, and to guard against radiation.

Temperatures were read to 0°.0001. The whole apparatus was carefully calibrated, and its various heat constants determined. The solution, previously brought to room temperature, was introduced into the apparatus, the stirrer set in motion and, after a few minutes, the temperature having become constant, the thermometer was read. The circuit was closed, and after 5 minutes was interrupted. The maximum temperature reached was nearly always read after 9 minutes.

Some non-electrolytes and poor electrolytes, as well as strong electrolytes, were studied. The relation between the hydration of a dissociated substance and the temperature coefficient of its heat of neutralization, and between hydration and temperature coefficients of heat of dilution, are also taken up.

Fuchs calls attention to the hypothesis of Puschl that the water which enters into combination has a lower specific heat than that which is free, and bases part of his calculations upon it. He finds that the hydrates of dissociated substances are combinations whose stability varies with the temperature, a

[1] Dissertation, University of Nancy.

conclusion also previously reached by Jones from his cryoscopic work.

The temperature coefficient of heat of neutralization, or of heat of dilution, is a function of the hydration of the substance, in fact, is proportional to the quantity of hydration. The coefficient is positive or negative, depending upon whether there is increase or decrease in the amount of combined water.

The author concludes that the specific heat of solution may be influenced by polymerization, by ionization and by the hydrating power of the substance.

His work shows, from a consideration of specific heats of solutions, that the non-electrolytes and poor electrolytes have, in general, small hydrating power. The compounds whose aqueous solutions are good conductors, on the other hand, have a great tendency to form hydrates when dissociated. This result confirms that obtained by Jones and Bassett through cryoscopic measurements. "The hydrating tendency of the good electrolytes increases with dilution as the law of mass action would lead us to expect." This result also is confirmatory of the results obtained by Jones and his co-workers.

The neutral molecules and the ions of weak bases and weak acids, as well as the hydrogen and hydroxyl ions, according to Fuchs, hydrate much less than the anions of strong acids and the cations of strong bases. It follows, therefore, that the affinity of a substance for the solvent by which it is ionized is not the sole cause of dissociation, as Auwers and his pupils contend. As examples are cited, trichloracetic acid which does not form hydrates, and the organic ammonium salts which have very little affinity for water; the ionization of these bodies being as strong as that of the other good electrolytes.

The alcoholates are of considerable complexity, consequently, the variation of the heat of neutralization in alcoholic solutions with the temperature is large.

Fuchs also studies the conductivities of certain substances with a view to ascertaining the effect of hydration, since the weak electrolytes have little affinity for water when compared with the strong electrolytes. He finds that the ionic velocities of the weak electrolytes remain constant with change in dilution, while that of the strong electrolytes diminishes as the dilution increases. This conclusion is in accord with the results obtained by the aid of the specific heats of solutions, when the hydration is taken into account. The author attributes the failure of Ostwald's formula: $\frac{\alpha^2}{(1-\alpha)v} = C$, to hold for strong electrolytes, to the modifying effects of hydra-

tion. This follows directly from Jones' idea that the mobility of the ion depends upon the amount of water attached to it, *i. e.*, the greater the hydration the more the freedom of movement of the ion is interfered with. C. M. STINE.

## REVIEWS.

ANALYSE DES MÉTAUX PAR ÉLECTROLYSE, par A. HOLLARD, Docteur ès-sciences, Chef du Laboratoire Central des Usines de la Cie Fse des Métaux, and L. BERTIAUX, essayeur du commerce. Paris: H. Dunod et E. Pinat, Éditeurs. 1906. pp. 180. Price, 6 Fr.

This work, as is stated in the preface, is not a compilation of the publications of a number of workers, but is the result of a dozen years of synthetical and analytical experiments by the authors. They have not only tested the methods synthetically, with known weights and mixtures, but have applied them to the analytical separation and detection of a variety of substances, such as minerals, alloys and commercial products. They also include in this volume an explanation of the theory of analysis by electrolysis, thus not only offering an interpretation of these complex phenomena, but also furnishing a guide for those who wish to carry on investigations in this general field. The authors have worked out a rational method of arrangement of the metals according to their behavior in determinations or separations by electrolytic methods; this, together with the principles upon which these separations are based, occupies Part I of the work. Part II contains the processes for determining the individual metals or of separating them from one another. In Part III the methods of analysis of minerals, alloys, etc., is given and in the fourth part the tables containing records of the experiments and the degree of accuracy of the determinations.

The authors have studied the conditions under which the metals can be deposited by electrolysis and have devised methods by which metals, whose properties are very similar, can be separated. They find, for example, that while zinc and cadmium cannot be separated if a platinum electrode is used, owing to the fact that the solution tension is so nearly equal, by using a cadmium cathode the tension of the hydrogen, which varies with the metal constituting the cathode, is between that of the two metals, and the one which shows the lowest tension is precipitated alone, in a strongly acid solution. They point out that while the metals cannot be classed according to the scheme followed in their qualitative separation they can be divided, according to their solution ten-

sion, into a group which can and one which cannot be deposited in a strongly acid solution. In each case all the details are given, so that there should be no difficulty in following the exact procedure recommended. Methods are described by which the different impurities in commercial metals can be determined with great accuracy by electrolytic methods. In examining this book one is impressed with the thoroughness with which the ground has been covered. Because of their accuracy and greater speed, these electrolytic processes will, without doubt, displace the older methods, especially in commercial laboratories, when time is an important factor.

J. E. G.

PREMIER CONGRÈS INTERNATIONAL POUR L'ÉTUDE DE LA RADIOLOGIE ET DE L'IONISATION; Tenu a Liége du 12 au 14 Septembre, 1905. Comptes rendus. Paris: H. Dunod et E. Pinat, Éditeurs. 1906. pp. 560. Price, $3.50.

The congress, the proceedings of which are here reported, is in some respects the most remarkable that has ever been held in connection with any scientific subject. It had to do chiefly with the subject of radioactivity in the broad sense. When it is recalled that this whole subject was first opened up only a comparatively few years ago by the discovery of the radioactivity of uranium by Becquerel, the unique character of a special conference being called to deal with radioactive problems becomes manifest.

The substance which, of course, is most important in this connection is radium, and radium was discovered only 3 or 4 years ago by the Curies. Further, the total amount of radium compounds, of a fair degree of purity, which has thus far been isolated, is a comparatively few grams.

When these two facts are taken into account, the significance of a special congress to consider the phenomena presented by this substance dawns upon us. The properties of radium and other radioactive bodies are so remarkable, and so different from those possessed by any other known substances, that although only a few grams of its salts have been isolated, it has seemed desirable to call a special meeting of physicists to discuss them.

As will be seen from the title of the "Report" the meeting was held in Liége from the 12th to the 14th of September, 1905. A large number of the leading physicists were present, and several papers of unusual interest were presented. Some of the more important are:

The increase in the conductivity of dielectrics when subjected to the action of the radium radiation, by Prof. Righi.

The analysis of the radiation of radioactive substances, by Prof. Becquerel.

A new radioactive element, radiothorium, which gives the same emanation as thorium, by Prof. Ramsay.

Some quantitative determinations of the heat evolved by radium, by Prof. Ångström.

Properties of condensation nuclei and their atmospheric distribution, by Prof. Barus.

On the ultimate disintegration products of the radioactive elements, by Prof. Boltwood.

The physiological action of radium was given considerable prominence at this congress. In this connection should be mentioned especially the papers by Prof. Dubois, Dr. Darier, Dr. Halkin and Prof. Lassar.

It should be noted that not only has a special congress been called to study the phenomena of radioactivity, but a special journal (*La Radium*) is now being published, in which the results of work in this field are being recorded. Such developments as these have no parallel in the history of Physical Science. H. C. J.

THE ELEMENTS OF CHEMICAL ENGINEERING. By J. GROSSMAN. With a Preface by SIR WILLIAM RAMSAY. London: Chas. Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co. 1906. pp. VIII + 152. Price, $1.50 net.

In this little book the author has attempted the difficult feat of condensing, within a small volume, the elements of chemical engineering. A brief course on this subject is much needed, for few technical schools allow sufficient time in their curricula for the study of the larger works, *e. g.*, that of Davis. The author assumes that the reader has some knowledge of chemical technology (*e. g.*, *vide* p. 49). Granting this, it seems to the reviewer that there is unnecessary diffuseness of statement in many cases, though in others, clearness of expression and description have been sacrificed to brevity. Also, some of the material presented bears the impress of the kindergarten method of instruction. This last, however, may appeal to many teachers into whose hands the book will come, as the best way of awakening the interest of the student. An examination of the material presented, reveals much valuable information, especially in Chapters X and XI, upon the Materials Used in Chemical Engineering, and on the Design of Plant. The discussion of Application of Heat, and Fuel, is excellent, as far as it goes, but is all too brief. A misprint on page 33 (balls for *bells*), leads to some obscurity of meaning. With certain further additions of purely engineering topics, *e. g.*,

pumps, fans, shafting, etc., the excision of verbiage and a more extended treatment of the subjects presented, a most useful book to the teacher and student will result.

F. H. THORP.

SECHS VORTRÄGE ÜBER DAS THERMODYNAMISCHE POTENTIAL, U. S. W., von J. J. VAN LAAR. Braunschweig: Vieweg und Sohn, 1906. Price, M. 3.50.

This small volume of 119 pages contains 6 lectures on the thermodynamic potential and its applications to problems of equilibrium in the fields of chemistry and physics, together with 2 lectures on concentrated solutions and on osmotic pressure. The work is of great interest and is strongly recommended to all students, especially to those working in chemistry. The volume contains little that is new, but the manner of presentation is clear and attractive. The great importance of the book comes from the attention it draws to the work of Van der Waals on the thermodynamic potential of liquids and its extension to include the case of concentrated solutions. The author emphasizes throughout the work the importance of the idea of a thermodynamic potential as introduced by Gibbs, and shows how the term osmotic pressure is limited in its usefulness and often leads to serious errors. It would be of the greatest advantage to all students of chemistry, whether in the field of physical chemistry or not, if they could receive a course of lectures based upon this work. J. S. A.

GENERAL PRINCIPLES OF ORGANIC SYNTHESES. By P. ALEXEVEFF, late Professor of Chemistry, University of Kieff. Authorized translation with revision and additions by J. MERRITT MATTHEWS, PH.D. First edition. First thousand. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1906. pp. VIII + 246. Price, $3.00.

The object and scope of this book are best set forth by the following extracts from the translator's preface: " * * * in this volume, I have made rather extensive additions of new material, together with a general rearrangement of the entire subject-matter. * * * This book is intended for the general student of advanced organic chemistry, and deals only with the theory of the subject. * * * The attempt of the author has been to present the theory of organic radicles in a systematic form and in as logical a method of development as possible, so that the student may acquire a comprehensive grasp of the general principles underlying synthetic organic chemistry." Any work which will contribute to the help of students along these lines is sure of a hearty welcome from all teachers of the subject. Unfortunately, the present volume is not of this character, and it can hardly fail to do harm to

any student who reads it. This verdict is based on the following grounds: The book shows many signs of lack of careful construction and revision, and for these the translator must be responsible because Professor Alexeyeff died some years before the translation was commenced. Pages are disfigured by obvious defects in proof-reading and by lengthy foot-notes. The legitimate use of a foot-note is well understood; unfortunately they are often used by authors as a refuge from the trouble involved in welding into compact and clear form, matter which occurs to them at intervals in the course of their work, so the later idea is put in a foot-note. Now it is not fair to expect *any* reader, and least of all a student, to buy a book and then do the author's thinking for him, yet this is often necessary in the volume under consideration. One instance will suffice: The foot-note on page 3 contains an utterly erroneous statement which is wholly incompatible with one on the same subject in the text on page 5. The statement about ketones on the same page is, to say the least, very badly expressed. Two further examples of great lack of care may be given: On pages 6 and 7 a table of possible oxidation derivatives of propane is given, distinction being made between those which are known and those which have not hitherto been prepared, but the table has been quoted, *without revision*, from a book published 16 years ago! Again, camphoric acid is stated (page 21) not to be "a dibasic acid, but a compound of alcohol, ketone and acid," and its extended formula is shown on this basis. The authority for such an interesting and startling statement is a paper by Friedel, published in 1889. The amount of work done on camphor and its derivatives since that date is relatively enormous, and to ignore it in this manner is inexcusable.

A word must be added about nomenclature. It is unfortunate that the translator appears to have adopted a system of his own, but even in the use of this he is inconsistent.

Less serious defects, though by no means to be passed over, are the use of the term "amido" when "amino" is meant, and the disfigurement of the pages with a shower of hyphens which are employed incorrectly.

There are other points that invite criticism but space will not permit of their enumeration; sufficient has, perhaps, been said to show that the book should not be allowed to fall into the hands of students, whom it could only confuse and mislead, while to the more expert chemist it would hardly be useful.

The publishers have done their part well and the text betrays no very obvious signs of being a translation.

J. Bishop Tingle.